

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 ($\Delta\bar{\nu}_{1/2}^{\text{ph}}$) 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.

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1. Introduction

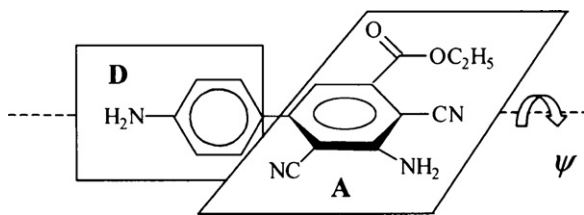
Molecules with polarity-sensitive spectroscopic properties are very useful in photochemical and photobiological studies for the understanding of microscopic solvent environments [1–5]. Such fluorophores are obviously most useful as optical probes when small perturbations cause large changes in spectroscopic 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 photo-

chemical 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 Boltzmann'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:

$$R = f\mu_g, \quad (1)$$

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]:

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

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]:

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

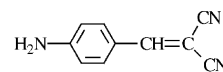
where

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

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: $\text{H}_3\text{C}-\text{CO}-\text{C}(\text{O})\text{OC}_2\text{H}_5$ and $\text{CH}_2(\text{CN})_2$ 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-

fied by column chromatography using silica gel, 70–230 mesh, as the stationary phase, with chloroform/ethanol (9:1) as eluent.

Yield: 55%, $^1\text{H NMR}$ ($(\text{CD}_3)_2\text{SO}$); δ 1.290–1.360 (t, 3H, $-\text{CH}_3$), δ 4.303–4.409 (q, 2H, $-\text{C}(\text{O})\text{O}-\text{CH}_2-$), δ 5.697 (s, 2H, $-\text{NH}_2$), δ 6.648 (s, 2H, $-\text{NH}_2$), δ 6.690–6.723 (d, $J=8.6$ Hz, 2H, aromatic), δ 7.165 (s, 1H, aromatic), δ 7.302–7.344 (d, $J=8.4$ Hz, 2H, aromatic).

The solvent used in the present study (tetrahydrofuran, THF) was the spectroscopic grade and was used without any additional purification. Absorption, excitation and luminescence spectra at room temperature and 77 K were recorded using, respectively, a Shimadzu UV-2401 PC spectrophotometer and a Shimadzu RF-5301 spectrofluorometer with 5.0 nm band-widths in both excitation and emission. For the measurements at room temperature (293 K) rectangular Suprasil 2 and 10 mm cells were used, whereas for these at 77 K suprasil tubes (3 mm in diameter) inserted into liquid nitrogen comprised in the finger of the quartz dewar were applied.

4. Results and discussion

Fig. 1 shows the long-wavelength absorption band and fluorescence excitation spectra (detecting at 505 nm) of EAADCy dissolved in THF, measured at 77 and 293 K. EAADCy shows structureless, broad, room-temperature long-wavelength absorption spectrum whose λ_{max} is situated at 404 nm and consists of at least two overlapping components. The excitation and absorption spectra are not superimposable. The differences between the absorption and excitation spectra of molecule under study show the existence of excited molecules in different spatial conformations. The long-wavelength excitation bands of EAADCy, obtained at 293 and 77 K, are composed of at least two bands, centered at about 370 and 430 nm. At room temperature the short-wavelength absorption maximum ($\lambda \cong 370$ nm) is more intense than that at $\lambda \cong 430$ nm. At 77 K the two intensity maxima show the reverse behavior. It has been shown in our previous paper [6] that conformers with donor and acceptor groups coplanar absorb and emit at wavelengths that are longer than those observed for molecules where the donor-acceptor groups are oriented orthogonally.

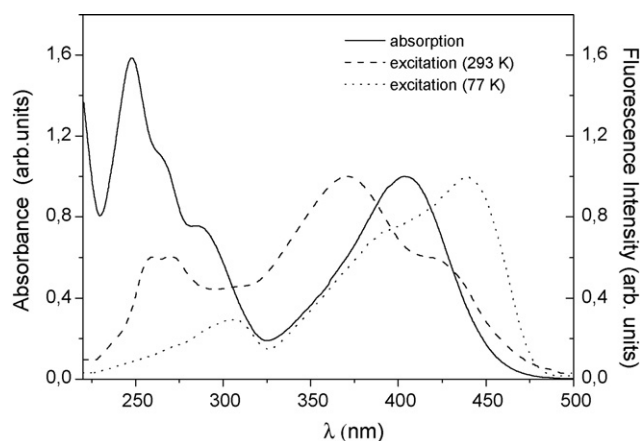


Fig. 1. Absorption and fluorescence excitation spectra at 293 and 77 K of EAADCy in THF.

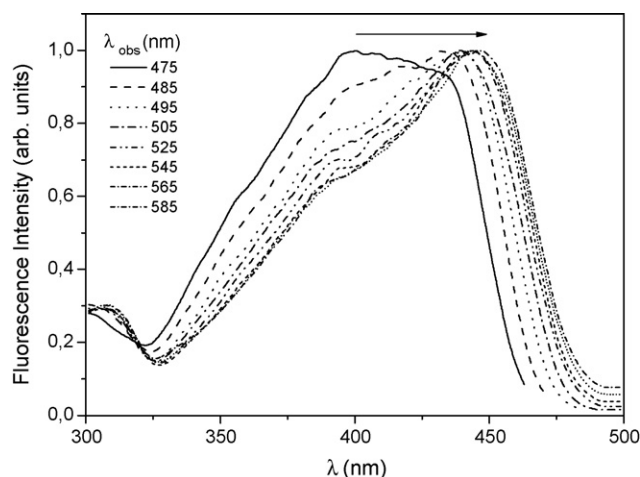


Fig. 2. The fluorescence excitation spectra of EAADCy in THF at 77 K as a function of λ_{obs} .

To obtain more information about the spectra of the two distinguishable species, we determined the fluorescence excitation spectra in THF glass at 77 K, under conditions where majority of molecular motions should be frozen. Fluorescence excitation spectra were carried out by detection at different wavelength of the emission spectrum (Fig. 2). We found that the fluorescence excitation spectra depend on the detecting wavelength of the emission spectrum. The low temperature excitation spectrum monitored at 475 nm (this wavelength correspond to the room temperature short-wavelength emission band) shows structureless broad spectrum whose $\lambda_{\text{max}}^{\text{exc}}$ is located at 398 nm and $\lambda_{\text{max}2}^{\text{exc}} \cong 450$ nm. Both bands show successive red shift when monitoring wavelength was shifted to longer wavelength. Upon increasing the observation wavelength, the intensity of short-wavelength band of the excitation spectrum at 370 nm decreases. This behavior is accompanied by an increase of the long-wavelength excitation band at 430 nm intensity. On the background of this effect there are the signatures of existence of molecules of different geometries (planar and perpendicular conformers).

The steady-state emission properties of EAADCy are also strongly solvent dependent (Fig. 3B). The low temperature (77 K) luminescence (fluorescence and phosphorescence) spectra of molecule under study were recorded in THF. Fig. 3A shows the long-wavelength fluorescence excitation (77 K), fluorescence (293 K), luminescence (77 K), and phosphorescence (77 K) spectra of EAADCy. As it is shown in Fig. 3A, at room temperature, the fluorescence spectrum of EAADCy in THF is double in character. 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 can be attributed to the emission from a singlet excited state of molecule in which two moieties are coplanar. It is noteworthy that at 77 K the molecule under study emits single but broad luminescence band whose λ_{max} is positioned at 500 nm (see Fig. 3A), which can be assigned mainly to fluorescence of the perpendicular form of EAADCy (in frozen THF the perpendicular form of molecule under study is the domi-

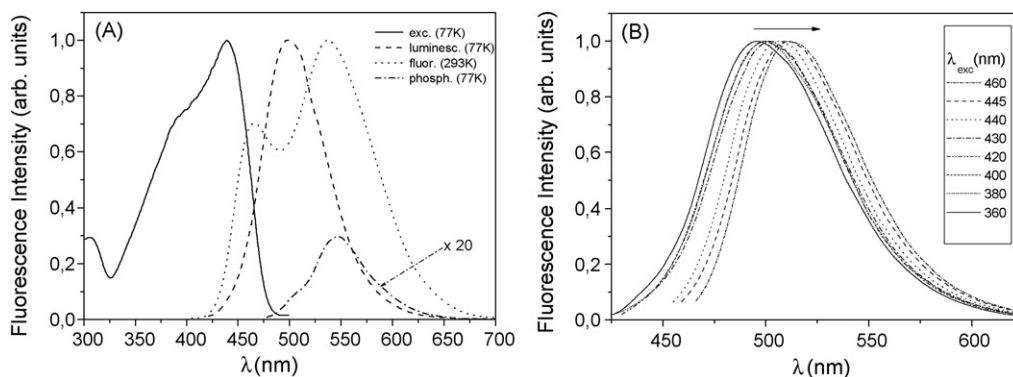


Fig. 3. (A) The long-wavelength fluorescence excitation band (77 K), fluorescence at 293 and 77 K and phosphorescence spectra of EAADCy in THF. (B) Normalized fluorescence spectra of EAADCy in THF at 77 K as a function of λ_{exc} .

nant species). These interesting spectroscopic features are in fair agreement with semiempirical computational predictions. The electronic energy value of the S_0 state obtained for different dihedral angle between two fragments of the investigated molecule (donor-D and acceptor-A) show that the most probable structure for the molecule under study is for 90° (perpendicular geometric structure of the D/A) [6]. At low temperature the luminescence radiation, besides the fluorescence, possesses a phosphorescence component with an intensity two order of magnitude smaller than that of the fluorescence (see Fig. 3A).

In general, fluorescence emission of molecules is governed by Kasha's rule which states that fluorescence normally occurs from the lowest vibrational level of the first excited electronic state. It is obvious from this rule that fluorescence should be independent on the excitation wavelength. It was shown in our previous paper [6] that, at room temperature, EAADCy exhibits significant fluorescence intensity distribution dependent on the λ_{exc} . This behavior indicate that molecule under study forms a typically spectrally inhomogeneous system (different conformers).

The luminescence spectra of EAADCy in THF glass at 77 K show considerable dependence on the excitation wavelengths (Fig. 3B and Table 1). The shift in luminescence maximum as a function of excitation wavelength is shown in Fig. 4. The position of emission maximum of EAADCy does not substan-

tially change when the excitation wavelength is changed from 340 to 415 nm. On the other hand, as the excitation wavelength is gradually shifted toward longer wavelengths, the emission maxima showed a concomitant red shift. As the excitation wavelength is changed from 340 to 455 nm, the emission maxima are shifted from 497 to 511 nm. Such dependence of the wavelength of maximum intensity of emission spectrum on the excitation wavelength is a characteristic demonstration of the red-edge effect.

In addition to the edge excitation red shift observed for a low-temperature emission, a similar shift is observed also in phosphorescence (Table 1). The excitation dependence of the phosphorescence of EAADCy in THF at 77 K is visualized in Fig. 5. The phosphorescence spectrum (broad and lacking structure) undergoes a significant red shift when increasing the excitation wavelength. Phosphorescence measurements carried out with excitation at 380 or 460 nm produced phosphorescence spectra shifted by 17 nm from λ_{max} of 448–465 nm (Fig. 6A and Table 1). It is noteworthy, the λ -onsets of the phosphorescence spectra obtained for different excitation wavelengths are not equal (Fig. 5). It is important to note that the full width at half maximum of phosphorescence spectrum ($\Delta\tilde{\nu}_{1/2}^{ph}$) of EAADCy in glass THF strongly depend on the excitation wavelength. In order to make this behavior more evident the dependence of

Table 1

Dependence of the maximum of the fluorescence, phosphorescence and full width at half maximum of phosphorescence spectrum ($\Delta\tilde{\nu}_{1/2}^{ph}$) of EAADCy in THF (77 K)

λ_{exc} (nm)	λ_{fl}^{max} (nm)	λ_{ph}^{max} (nm)	$\Delta\tilde{\nu}_{1/2}^{ph}$ (cm^{-1})
460	511	564	1550
455	510	560	1580
445	508	558	1640
440	504	553	1680
430	501	550	1845
420	499	549	1950
410	500	551	1990
400	501	548	1970
380	499	548	1950
360	499	547	2000
340	497	545	2020
320	499	547	1950
300	498	548	2000

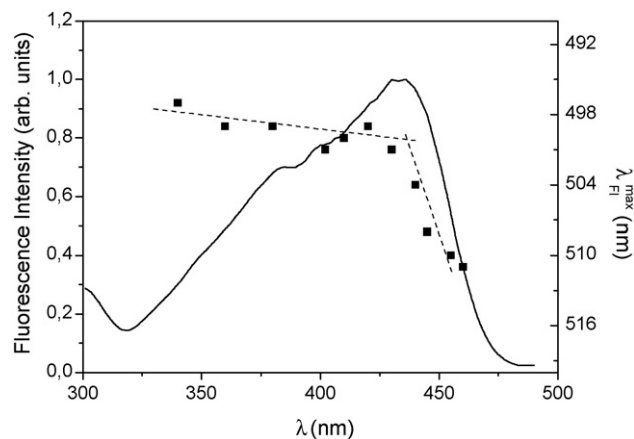


Fig. 4. The excitation wavelength dependence on the fluorescence intensity maximum position of EAADCy in THF (77 K). Excitation spectrum is given for comparison.

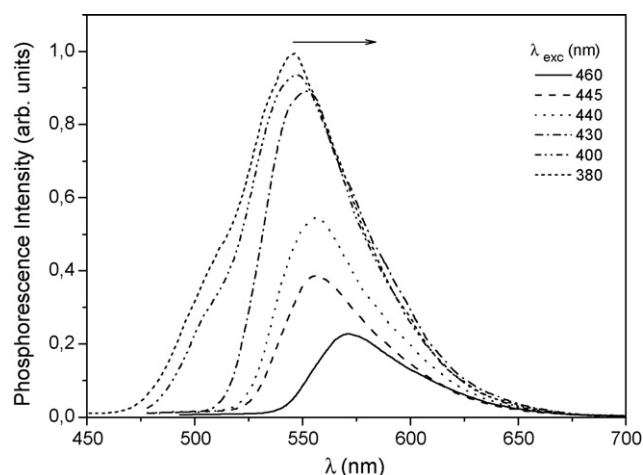


Fig. 5. The excitation wavelength dependence of the phosphorescence spectra of EAADCy in THF (77 K).

$\Delta\tilde{\nu}_{1/2}^{\text{ph}}$ versus the excitation wavelength is shown in Fig. 6B. The $\Delta\tilde{\nu}_{1/2}^{\text{ph}}$ decreases with increasing excitation wavelength from $2000 \pm 50 \text{ cm}^{-1}$ for excitation in the range of 275–420 nm to $1600 \pm 50 \text{ cm}^{-1}$ for excitation at 560 nm (Table 1).

For EAADCy, a distribution of rotational angles between donor and acceptor moieties is always present, and freezing the solvent may fix this distribution. Naturally, the different rotamers possess different energies (singlet and triplet states), and phosphorescence excitation dependence may be explained

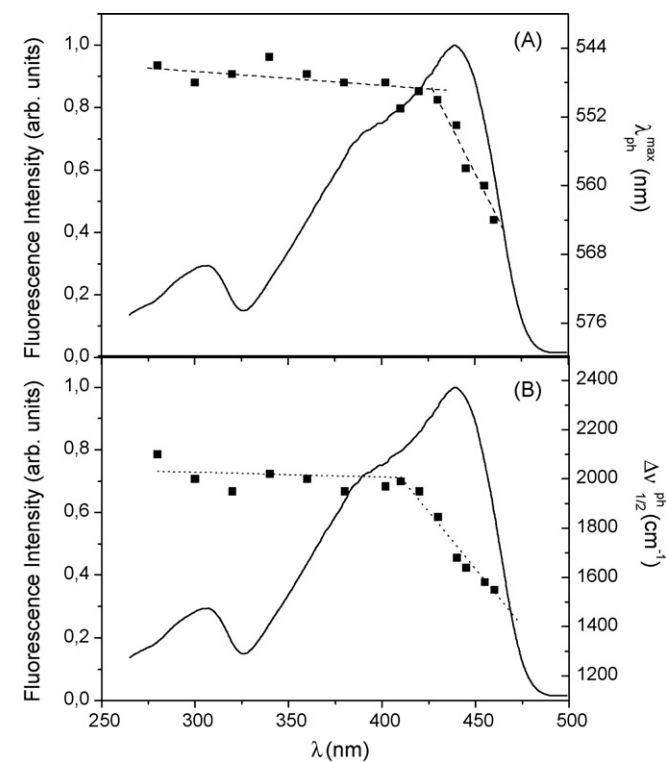


Fig. 6. The excitation wavelength dependence of the phosphorescence intensity maximum (A) and full width at half maximum of phosphorescence spectrum ($\Delta\tilde{\nu}_{1/2}^{\text{ph}}$) (B) of EAADCy in THF (77 K). Excitation spectrum is given for comparison.

by different rotamers that are present. The absorption and excitation spectrum of EAADCy in THF at 293 and 77 K is broadened by the overlapping of various absorption spectra due to the existence of various conformers. When the excitation is carried out at the maximum of the absorption band, the various conformers are excited (mainly perpendicular or nearly perpendicular conformers). As the excitation wavelength is shifted to the red, the rotamer with different angles ($90^\circ > \psi > 0^\circ$) between their interatomic planes is selectively excited. The energy of T_1 state of the conformer excited at the red edge of the absorption spectrum is lower than that of the conformer excited at the maximum of the absorption band, so that the phosphorescence spectrum shifts to the red.

As it was mentioned earlier, the width of inhomogeneous broadening function ($\Delta\tilde{\nu}_{\text{inh}}$) depends on the solvent polarity, and most importantly, on the change of the fluorophore dipole moment on excitation. In our previous publication [6], the ground (μ_g) and excited (μ_e) state dipole moments of planar and perpendicular form of molecule under study were estimated from solvatochromic shifts of absorption and fluorescence spectra as a function of the dielectric constant (ϵ) and refractive index (n). It is important to note here, that the planar form of EAADCy possesses greater dipole moment in the excited state than in the ground state, while perpendicular form of EAADCy possesses lower dipole moment value in the excited state in comparison to its value in the ground state. The following changes of dipole moment were obtained: $\Delta\mu_{\text{perpen}} = -1.82 \text{ D}$, $\Delta\mu_{\text{planar}} = 13.5 \text{ D}$. The Onsager cavity radius of EAADCy was calculated (using optimized geometry) to be 8.5 \AA . Using Eq. (3), for EAADCy dissolved in THF the estimated value of $\Delta\tilde{\nu}_{\text{inh}}$ at room temperature is about $900, \sim 100 \text{ cm}^{-1}$ and it decreases to $350, \sim 50 \text{ cm}^{-1}$ at 77 K for planar and perpendicular form, respectively.

5. Conclusions

In order to understand why EAADCy exhibits significant red-edge effect, it is important to take into consideration the possibility of photoselection of the different conformers of EAADCy molecule during excitation. As the excitation wavelength is changed, a slightly different species are excited and an emission characteristic for these particular species is observed. On excitation with shorter wavelengths different conformers (possess different rotation angles between donor and acceptor moieties) of EAADCy are excited and the longer wavelengths of excitation mainly molecules with coplanar conformations are excited. It was shown that the S_0 – S_1 transition energy of the planar form is smaller than transition energy of the perpendicular form, so that the rotamer selected at the red-edge excitation is mainly assigned as the planar form. Similarly to fluorescence spectra, inhomogeneous broadening causes the long-wavelength shifts of phosphorescence spectra at the red-edge excitation in THF glass.

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