Experimental and theoretical studies of the influence of solvent polarity on the spectral properties of two push-pull oxazol-5-(4H)-one compounds

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ABSTRACT

Spectral and photophysical properties of two derivatives of the 2-phenyl-1,3-oxazol-5(4H)-ones were studied in 17 solvents of different polarity. These compounds have either push-pull non-centrosymmetric or C_3-symmetric structures with electron-withdrawing groups (2-phenyl-oxazolone) introduced onto the triphenylamine. It has been found that their spectral and photophysical properties depend on the structure of the compounds and on the solvent polarity. The non-radiative relaxation process is facilitated by an increase of the solvent polarity. The changes in the electronic absorption and fluorescence maximum positions with solvent polarity were analyzed applying different solvent polarity parameters based on Lippert-Mataga, McRae, Bakhshiev and Kawski theories or E_T^N scale. The long-wavelength absorption band positions exhibit a slight dependence on the solvent, whereas the fluorescence spectra demonstrate substantial positive solvatochromism. It was found that the position of the electronic absorption band depends mainly on the solute polarizability (related to the solvent refraction index function $f(n^2) = (n^2–1) / (2n^2 + 1)$), whereas the solvent polarity influences the position of the fluorescence band. Quantum chemical calculations of the transition energies and dipole moments at the DFT level have been also performed. The difference between the first excited and ground state dipole moments was found experimentally to be 10.8 D and 13.0 D according to Bakhshiev's model. The experimental values of $\Delta\mu$ were compared to that one obtained from theoretical calculations for various solvents.

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1. Introduction

Organic dyes, which have been synthesized based on different heterocycles, have been extensively studied for their application in many fields of chemistry, biology and industry. Among them polymethine compounds are very important due to tunability of their spectral properties by a change in their chemical structure [1]. Most of the dyes are derived from five- and six-membered rings containing one or more nitrogen heteroatoms, with the rings being fused into another aromatic ring [2]. A valuable chemical intermediate in the synthesis of push-pull organic dyes is the oxazol-5-(4H)-one. The simplest heterocyclic dyes containing oxazolone moiety are prepared by the reaction of aromatic aldehydes with hippuric acid in a dry acetic anhydride catalyzed by sodium acetate [3]. The synthesis was firstly described by Plöchl in 1883 [4]. Since that, various reagents and catalysts, such as, KF/NaOAc [5], Al_2O_3-H_3BO_3 [6], Bi(III) salts [7], Pb(OAc)$_2$ [8] and ZnO [9] were used to form different classes of the 5(4H)-oxazolone derivatives [10].

Since the photophysical and photochemical properties [11], of the oxazolone derivatives vary with their structure, they found widespread application, e.g. in medicine. They have distinctive biological activities like anti-bacterial [12–14], anti-HIV [15], antifungal [16], anticancer [17], anti-diabetic, antitumor, antagonistic, sedative [18–20] and cardiotonic activity [21]. They are also used as synthons for the design of various biosensors [22,23], fluorophores [24], electrophotographic photoreceptors and in non-linear optical materials [25–27].

For some of the applications, dyes should have a dipolar structure bearing electron donating substituent linked to the oxazolone skeleton (electron acceptor) by a π-conjugated bridge. Such structure is conducive to intramolecular charge transfer (ICT) and promotes the redshift of the absorption and fluorescence bands position [28]. Since the strength of ICT depends on the solvent used, understanding the links between molecular structure, solvent polarity and photophysical properties of the dyes is crucial.

Depending on the solvent, the shift of the position of absorption and fluorescence bands arises from either specific or non-specific solute-solvent interaction [29]. The common example of the specific interaction is e.g. hydrogen-bonding. The effect results from anisotropic

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interactions between the chromophore and one or more solvent molecules in its solvation shell [30]. In non-specific interactions the solvent is assumed to act as a continuous dielectric medium [31]. Thus, the solvent effect on the spectral shifts can be assessed using different polarity scales and solvatochromic parameters taking into account the solvent dipolarity/polarizability, hydrogen bond donor strength and hydrogen bond acceptor strength [32,33]. Among them one of the most popular polarity scale is E_T^N [33,34]. This scale uses the polarity extremes of water and tetramethylsilane (TMS) as reference solvents. Therefore, solvents can be devided into three groups: protic (E_T^N from 0.5 to 1), dipolar non-hydrogen donating (E_T^N from 0.3 to 0.5) and apolar (E_T^N from 0 to 0.3). Ploting the Stokes shift vs. the microscopic solvent polarity parameter, E_T^N, we are able to calculate the dipole moment change between the excited and ground state [31,35,36]. Additionally, spectral and photophysical properties of the solute can be analyzed applying multi-linear correlation using the three-parameter solvents scales of Kamlet-Taft [37,38] and Catalán [32,39] or four-parameter Catalán [40] solvent scale.

The solvent effect on the position of absorption and fluorescence bands can be applied to estimate the change in the dipole moments between ground and excited state which reflects the charge distribution in the molecule. Absorption of a photon by a molecule causes a change in electron density. This can result in an increase or decrease of dipole moment of the excited state as compared to the ground state. The excited state dipole moment can be determined based on the spectral shift caused by either electrochromism or solvatochromism. Commonly used, solvatochromic methods are based on Lippert [41], Mataga [42], McRae [43], Bakhshiev [44], and Kawski [45] theories including the Onsager description of non-specific electrostatic solute-solvent interactions. They lead, in spite of different assumptions, to similar expressions for the difference between the absorption and fluorescence bands positions of the solute in different solvents ($\nu_{ab} - \nu_{fl}$):

$$\nu_{ab} - \nu_{fl} = m_1 \cdot f(\varepsilon, n) + const \tag{1}$$

where

$$m_1 = \frac{\left(\vec{\mu}_e - \vec{\mu}_g\right)^2}{2\pi\varepsilon_0 h c a^3} \tag{2}$$

where: the parameter m_1 is the slope of the straight line (in cm^{-1}), μ_e and μ_g are the dipole moments in the excited and ground states, respectively, h is Planck's constant, c is the velocity of light in vacuum and a is Onsager's interaction radius of the solute (in Å). The $f(\varepsilon, n)$ is the solvent polarity parameter which differs significantly in the particular theories [45,46]. Finally, the dipole moment difference between the ground and the excited states is given as:

$$\Delta\mu = 3,3325 \cdot 10^{-32} \text{Cm} \cdot \left[a^3 m_1\right]^{0.5} \tag{3}$$

where: $1D = 3.33564 \cdot 10^{-30}$ Cm.

The present study was undertaken in order to characterize the solvatochromic properties of two oxazolone derivatives with respect to their structure. The experimental results are supplemented with theoretical simulations.

2. Experimental section

The synthesis of the tested compounds, (4Z)-4-[4-(diphenylamino)benzylidene]-2-phenyl-1,3-oxazol-5(4H)-one (4) and (4Z)-N,N,N-tris[2-phenyl-4-benzylidene-1,3-oxazol-5(4H)-one]amine (5) is described in our previous paper [28]. Their structures are presented in Chart 1.

All solvents (spectroscopic grade) were purchased from Aldrich Chemical co. and were used as received. The solvent parameters applied for the calculations, the values of solvent polarity functions and their
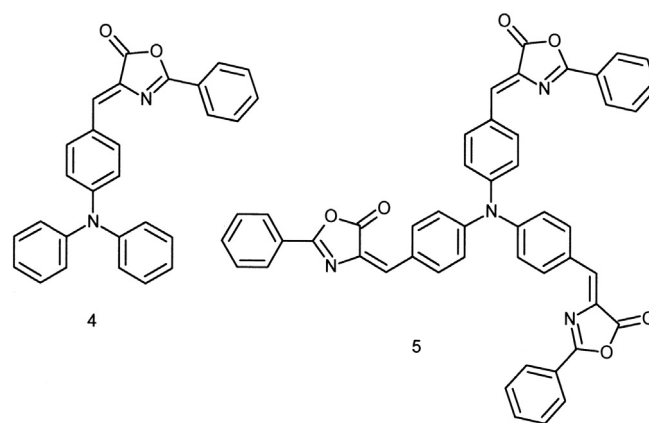

Chart 1. Chemical structures of the compounds under the study.

relative permittivities (ε) and refractive indexes (n) at 20 °C [34] are compiled in Table S1.

The steady-state absorption and emission spectra were recorded at room temperature using a Shimadzu UV–vis Multispec-1501 spectrophotometer and a Hitachi F-4500 spectrofluorimeter, respectively. The solutions were prepared in solvents of different polarity with a concentration of the dye in the solution 1.0×10^{-5} M and 1.0×10^{-6} M, respectively.

The fluorescence quantum yields for the dyes in different solvents were calculated using Eq. (4). The absorbances (A) of both the dye and reference solution at an excitation wavelength (470 nm) was ca. 0.1. Fluoresceine in 0.1 M NaOH ($\phi_{ref} = 0.91$ [47]) was used as reference.

$$\phi_{dye} = \phi_{ref} \frac{I_{dye} A_{ref}}{I_{ref} A_{dye}} \cdot \frac{n_{dye}^2}{n_{ref}^2} \tag{4}$$

where: I_{dye} and I_{ref} are the integrated emission intensity, n_{dye} and n_{ref} are the refractive indexes of the solvents used for the dyes and the reference, respectively.

The fluorescence lifetimes were measured using a time-correlated single photon counting (TCSPC) system (FLS920P Spectrometers). The samples were excited at 466 nm using a picosecond diode laser (Edinburgh Instruments) generating pulses of about 81.5 ps. Its maximal average power is 5 mW. Short laser pulses in combination with a fast microchannel plate photodetector and ultrafast electronics make a successful analysis of fluorescence decay signals with a resolution of few picoseconds possible. The instrument response function was obtained by water in a quartz cuvette. The fluorescence decays were deconvoluted using FAST software. The fluorescence decays were fitted to bi-exponentials. The average lifetime, τ_{av} is calculated as $\tau_{av} = (\Sigma_i \alpha_i \tau_i) / (\Sigma_i \alpha_i)$, where α_i and τ_i are the amplitudes and lifetimes.

The solvent effect on the spectral properties of tested dyes was analyzed based on one parameter scale, E_T^N. The shift between the absorption and fluorescence maxima as a function of solvent polarity parameter was applied to determine the dipole moment of the solute in the excited state. The Lippert-Mataga [41,42], Bilot and Kawski [45], McRae's [43], Bakhshiev's [44,48] and Kawski-Chamma-Viallet's [45,49] equations were used for the calculation. These methods are based on a dielectric continuum description of the solvent and the classical Onsager cavity model.

2.1. Theoretical aspect

Quantum chemical calculations were carried out using the Gaussian 09 program [50] package. Geometry optimization of the molecules in the ground state was performed at the B3LYP/6-311++G(d,p) level both in vacuo and with the inclusion of solvent effects by applying the