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Factors that influence the spectroscopic properties of 1,3-bis[*p*-substituted-(phenylamino)]squaraines

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ABSTRACT

The spectroscopic characteristics of a series of ten aminosquaraine dyes that differ in the type of chemical substituent at the *p*-position of the phenyl ring were investigated. The effect of solvent on the properties of the dyes in their ground and excited state is described. The absorption and emission properties, fluorescence lifetime and rate constants for radiative and non-radiative deactivation processes are also presented. The dyes displayed very short fluorescence lifetimes (about 3 ns) and dependence of the radiative deactivation process on the solvent viscosity.

1. Introduction

Squaraine dyes, first synthesised in the mid-1960s, consist of an oxocyclobutenolate core with aromatic or heterocyclic components at both ends of the molecule [1,2]. Many squaraines, possess polymethine structures with amine and iminium terminals. For this reason, these compounds are occasionally classified as cyanine dyes. 3,4-Dihydroxycyclobut-3-ene-1,2-dione is a core reactant in the synthesis of squaraine dyes [3,4]. Squaric acid is a diacid that exhibits two acidic hydroxyl groups with pK_a values of 0.54 and 3.48 as well as two highly polarised carbonyl groups [5]. This unique structure provides not only versatile proton acceptor sites at the carbonyl function, for hydrogen-bonding associations, but also binding sites to metal ions and other compounds [6–8] through the hydroxyl groups. The first synthesis of squaraine dyes was reported by Treibs and Jacob in 1965 [9]. This reaction involved the condensation of 3,4-dihydroxy-3-cyclobutene-1,2-dione with two equivalents of electron-rich aromatics such as α-unsubstituted pyrroles and 1,3,5-trihydroxybenzene under acidic conditions. Since then there have been many squaraine dyes possessing different heterocyclic or aromatic components [7,10,11]. Aniline-based squaraines were described for the first time in 1966 by Sprenger and Ziegenbein [12]. The treatment of 3,4-dihydroxycyclobut-3-ene-1,2-dione with two molar equivalents of primary or secondary amines avoids the formation of symmetrical squaraines, resulting in a double condensation reaction by the amine [7,13], commonly referred to as aminosquaraines. Aminosquaraines have also been synthesised by the isomerisation of squaric acid 1,2-diamides [7].

Squaraine dyes normally exhibit intense absorption and often fluorescence emission. They have attracted much attention from the viewpoint of technological applications. Generally, the spectroscopic properties of squaraine dyes depend on the chemical structure of the chromophore heterocyclic or aromatic component. Thus, efforts have been made to develop new synthetic methods for constructing squaraine-based chromophores. The search for such chromophores is still relevant due to the important practical applications of squaraines, including xerographic devices utilising the photoconductive properties of squaraine dyes, photovoltaic devices employing the dyes as photosensitisers, dyeing photoinitiating systems employing squaraines also as photosensitisers [14–16] and biolabeling and chemosensory materials for analytical uses. Low band-gap electroconductive materials are available by the polymerisation of squaraine skeletons, as well as supramolecular systems. Furthermore, it should be noted, that these dyes are attaining an increased importance in the field of supramolecular chemistry.

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These dyes have been applied in squaraine-based molecular sensors, self-assembly, in polymeric materials and biological applications [17,18]. The polymers containing squaraine moieties form a new class of low bands gap materials. For example, polyaminosquaraines have been examined as conducting polymers [19]. Moreover, in 2011, the crystal structure and study, from a supramolecular perspective, of other squaraines, e.g. anilinosquaraines, was described by Silva et al. [20].

The aminosquaraine dyes reported here were synthesised by the condensation reaction of squaric acid and a two molar equivalent of (*p*-substituted)anilines. A characteristic feature of these compounds is the position of the nitrogen atoms in the system of conjugated double bonds. The chemical structures of these aminosquaraine dyes, in particular the type of substituent on the phenyl rings, vary their excited state energetics and the electronic properties [19–22]. For example, as it has been shown by Park et al., slight modification of the squaraine structure by incorporating the aryl amine functional group directly through the nitrogen atom of the amino group to the squarate ring system results in drastically different optical responses [23]. Thus, the objective of these studies was the synthesis of a range of 1,3-aminosquaraine dyes with differing structures, and investigation of their light absorption and fluorescence properties. An understanding of the influence of substituents in the *p*-position of the phenyl rings on the excited state processes is very important in determining the photosensitivity of these squaraine dyes, which is presented also in this article.

2. Experimental

2.1. Materials and general methods

Squaraine dyes were synthesised by reaction of squaric acid with aniline and *p*-substituted anilines, by the general method described in the literature [23]. All reagents and solvents (spectroscopic grade) were purchased from Aldrich (Poland) and used without further purification.

Absorption and emission spectra were recorded at room temperature using an Agilent Technology UV–Vis Cary 60 Spectrophotometer, a Hitachi F-7000 spectrofluorimeter and UV–VIS–NIR Fluorolog 3 Spectrofluorimeter (Horiba Jobin Yvon), respectively. Spectra were recorded in the following solvents: water (H_2O), dimethylsulfoxide (DMSO), acetonitrile (CH_3CN), *N,N*-dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (MP), methanol (MeOH), ethanol (EtOH), acetone, tetrahydrofuran (THF) and diethyl ether. The final concentration of dye in solution was 1.0×10^{-5} M. Spectroscopic measurements were performed in the above mentioned solvents containing 20% of 1-methyl-2-pyrrolidinone. For this purpose a suitable amount of dye was dissolved in 1-methyl-2-pyrrolidinone, then 2 mL of the concentrated (ca. 1 mM) stock solution was added to a 10 mL volumetric flask containing spectroscopic grade solvents.

The fluorescence quantum yield for each dye in the solvents was determined as follows. The fluorescence spectrum of a diluted dye solution ($A \approx 0.1$ at 366 nm) was recorded by excitation at the maximum of the absorption band of the standard. Dilute Coumarin I ($\Phi = 0.64$ [25]) was used as a reference. The fluorescence spectra of Coumarin I was obtained by excitation at 366 nm. The fluorescence quantum yield of each dye (ϕ_{dye}) was calculated using equation (1):

$$\phi_{dye} = \phi_{ref} \cdot \frac{I_{dye} A_{ref}}{I_{ref} A_{dye}} \cdot \frac{n_{dye}^2}{n_{ref}^2} \tag{1}$$

where: ϕ_{ref} is the fluorescence quantum yield of the reference, A_{dye} and A_{ref} are the absorbances of dye and reference at the excitation wavelength, I_{dye} and I_{ref} are the integrated emission intensity for dye and reference, n_{dye} and n_{ref} are the refractive indexes of the solvents used to dissolve dye and reference, respectively.

Fluorescence lifetimes were measured using a single-photon counting UV–VIS–NIR Fluorolog 3 Spectrofluorimeter (Horiba Jobin Yvon). The apparatus utilises, for excitation, a picosecond diode laser generating pulses of about 55 ps at 370 nm. 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. Dyes were studied at a concentration able to provide the equivalent absorbance at 370 nm (0.2 in the 10 mm cell) to be obtained. Fluorescence decay was fitted to two exponentials.

3. Results and discussion

Ten aminosquaraines with structures presented in Fig. 1 were studied and have been described here.

The general procedure of synthesis of aminosquaraines was based on the condensation reaction of squaric acid with *p*-substituted aniline derivatives in a mixture of 1-butanol and toluene described in details by Part et al. [23].

The aminosquaraine dyes studied belong to a class of symmetric D–A–D (donor–acceptor–donor) compounds, and differ in the type of substituent in the *p*-position of the phenyl ring. The D–A–D arrangement of each dye molecule has an interesting effect on the formation of intramolecular charge-transfer states. Studies by Kamat et al. [21] on the photochemistry of 1,3-bis[4-(dimethylamino)phenyl]squaraine, and associated quantum chemical calculations, may suggest that 1,3-bis[*p*-substituted(phenylamino)] squaraines are highly polarised, with the *p*-substituted-phenylimino moiety being an electron donor (D) and the central C_4O_2 unit being an electron acceptor.

It is well known that the properties of ground and excited state compounds depend on the properties of the surrounding solvent. The molecules of a solvent may interact (electrostatic interactions, hydrogen bonding associations, Van der Waal interactions, etc.) with molecules of dissolved compounds. It is also well known that squaraines form a solute–solvent complex in organic solvents; the equilibrium constant of which is dependent on the D–A–D charge-transfer character of the particular squaraine [21]. Therefore, the effects of physicochemical properties of solvent on the properties of each aminosquaraine compound shown in Fig. 1, in its ground and excited state, were studied. The characteristic spectroscopic properties of each aminosquaraine dyes in a few solvents were also studied. The solvents used differed in both polarity and viscosity.

The absorption and emission spectra of the dyes under investigation in acetonitrile are shown in Figs. 2 and 3.

The spectral characteristics of the aminosquaraine dyes are summarised in Table 1.

The aminosquaraines under investigation have intense, sharp absorption bands in the visible region with absorption maxima ranging from 340 nm to 530 nm, and molar extinction coefficients varying from 0.16×10^4 M^{-1} cm^{-1} to 11.3×10^4 M^{-1} cm^{-1}. These molar extinction coefficients are low in comparison with most other squaraine dyes, but are still moderate to high in comparison with simple azo dyes. The position of the absorption band maximum and value of molar extinction coefficient for each dye depends on the dye structure and properties of solvent used. The majority of all aminosquaraine dyes tested, show an intensive yellow colour in all solvents used, with the exception of dye **SQ5**, which possesses a strong electron-withdrawing nitrogen group in the *p*-position of the phenyl rings. The absorption band of **SQ5** is red-shift in comparison to the other dyes studied (see data in