



Photochemical studies of new benzothiazole- and benzoselenazole-derived aminosquarylium dyes



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ABSTRACT

In this work, new modified squarylium dyes, namely two new groups of benzothiazole- and benzoselenazole-derived squarylium dyes, were studied. An extensive photochemical characterization of all dyes was performed and the following parameters were studied: quantum yields of singlet oxygen formation, fluorescence quantum yields and fluorescence lifetimes. Depending on the nature of the substituent located in the squaric ring, significant results were obtained. The laser flash photolysis technique was used to determine triplet–triplet absorption spectra, in ethanol. In chloroform, photoproducts resulting from a reaction of the excited squarylium dye in the singlet state with CHCl_3 were observed. A solute–solvent complex was detected, the primary product formed after excitation, being the complex $[\text{SQ}^+ \cdots \text{CHCl}_2 \cdots \text{Cl}^-]$. The effect of two different counterions (CF_3SO_3^- and I^-) was also addressed by these techniques providing new insights about the external heavy atom effect mechanism.

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1. Introduction

Squarylium dyes are known as functional dyes used as light absorbing materials in dye sensitized solar cells (DSSCs),¹ optical recording media,² nonlinear optical material,³ as fluorescent markers in bio-labeling, and as photosensitizers for photodynamic therapy of cancer (PDT).^{4,5} These applications will depend of specific photophysical and photochemical properties, namely fluorescence quantum yields and lifetimes, and singlet oxygen quantum yields. The latter involves the use of a sensitizer, which after being localized in the target tissue, gives rise, upon illumination, to a set of biochemical processes, which renders the destruction of the abnormal cells. Singlet oxygen, generated from ground-state triplet oxygen, will be the main cytotoxic species responsible for the biological effects.⁶ Besides that, for the majority of applications, the common key requirements are mainly related with high absorption at wavelengths in the UV–visible and/or near-infrared (NIR) range, and high chemical stability and solubility.

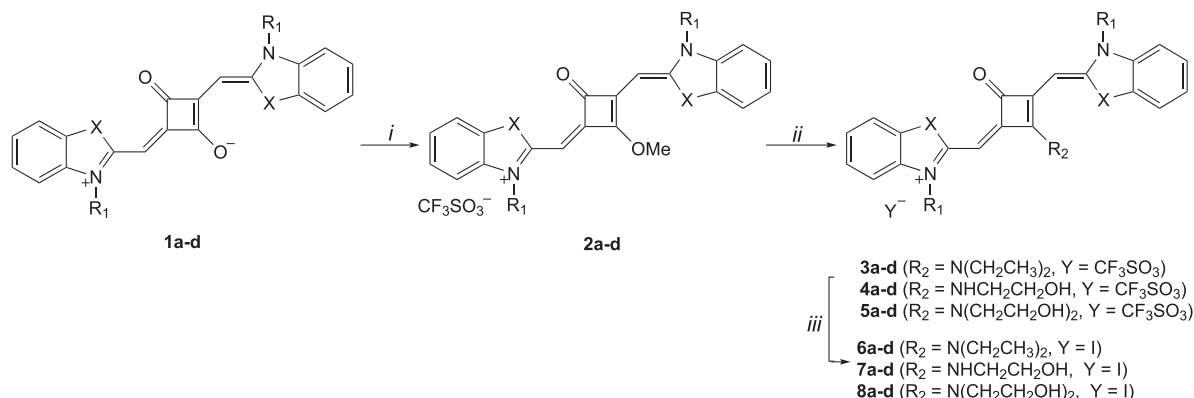
This class of cyanine dyes is distinguished by their good photochemical stability and sharp absorption with high extinction coefficients in the red and NIR region. In addition to that, it is also relevant to mention the relatively high fluorescence quantum

yields and lifetimes, significant quantum yield conversion of triplet oxygen to cytotoxic singlet oxygen, as well as the possibility of tailoring these photochemical properties with an appropriate dye functionalization.^{7–9} Thus, because of the unique properties of squarylium dyes, structural and chemical modifications have been an active area of research since these dyes were developed, by means of new and improved synthetic routes, which can provide new features taking into account the desired application. For instance, the inclusion of appropriate substituents onto the N-atom of the heterocyclic moiety in order to improve the dye's solubility, or, in more complex cases, the introduction of a heavy atom (sulfur or selenium) into the compound, which potentially enhances the singlet oxygen generation through the internal heavy atom effect.^{10,11} It is also known that modifying the effective electron releasing ability of the terminal groups, or polymethine bridge between them by introducing electron-withdrawing or donating groups at an appropriate position, for instance at the central four-membered ring, we can alter the π -system's resonance, resulting in a shift of the squaraine absorption spectrum. However, as it has been well documented, these modifications can also induce other phenomena that ultimately increase the non-radiative decay processes. Among those, it has been suggested that photoisomerization is the most significant pathway for deactivation, followed by internal conversion, for cyanine dyes.^{12–14} The level of photoisomerization depends on dye rigidity, and so, by introducing

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rigidifying structures or rotation-hindering bulky substituents, photoisomerization would be expected to decrease with the corresponding increase in the fluorescence quantum yields. The central squaric ring and the increase in the length of the dye's alkyl chain, are ultimately supposed to decrease the photoisomerization processes that compete directly with all radiative pathways, which

derivatives was readily achieved by methylation of the zwitterionic squarylium precursors **1** with methyl trifluoromethanesulfonate as described previously.³² Dyes **3–4**, which were obtained in fairly good yields, underwent counterion exchange by iodine upon treatment with a methanolic solution of KI to furnish dyes **6–8** (Scheme 1).



a: X = S, $R_1 = C_2H_5$; b: X = S, $R_1 = n-C_6H_{13}$; c: X = Se, $R_1 = C_2H_5$; d: X = Se, $R_1 = n-C_6H_{13}$

Scheme 1. Reagents and conditions. (i) $CF_3SO_3CH_3$, CH_2Cl_2 , N_2 , rt; (ii) $NH(CH_2CH_3)_2$ or $NH_2CH_2CH_2OH$ or $NH(CH_2CH_2OH)_2$, CH_2Cl_2 , N_2 , rt; (iii) 14% aq KI, rt.

are well known, for instance, in several carbocyanine dyes.^{15,16} However, regarding internal conversion processes, there are also studies that follow an intramolecular charge transfer (ICT) approach, which renders a fluorescence emission that is quenched by this effect. These squarylium dyes consist of two electron-donating end groups (D) and a central electron-withdrawing substituted unit (A) forming a donor–acceptor–donor (D–A–D) alignment, suggesting that both the ground state and the lowest excited singlet state of squaraines involve significant ICT, which is more significant in polar solvents, and that compete directly with the radiative deactivation processes.^{17–21}

There are some reports that point out to a modification of squarylium dyes into radical products by way of an intermediate complex that is formed in multiphotonic processes, with a solvent molecule or solvent radical. Also, it is also assumed that this photodegradation occurs in a much faster way in dichloromethane, chloroform, or halogenated solvents, than in alcohols,¹⁸ as we also discuss in this work.

Herein we report an extensive photophysical characterization of several squarylium cyanine dyes, displaying strong absorption between 600 and 700 nm, regarding their ability to generate singlet oxygen, their fluorescence quantum yields and lifetimes. The structural variations studied in this work concerned the nature of the heteroaromatic ring, the length of the *N,N*-dialkyl groups, and the type of functionalization of the squaric central ring. The external heavy atom effect was also addressed by directly comparing all photophysical parameters, regarding I^- and $CF_3SO_3^-$, the two counterions used in this case. The triplet state and the triplet–triplet absorption spectra were obtained by means of laser flash photolysis, which also provided the necessary information about the solute–solvent interaction, both in ethanol and in chloroform.

2. Results and discussion

2.1. Synthesis of the dyes

The key aminosquarylium dyes **3–5** were synthesized by nucleophilic substitution of the central methoxy group of the *O*-methyl derivatives **2** by appropriated amines. The preparation of the later

2.2. Ground state UV–visible spectral characterization

Fig. 1 exhibits the general structure of the squarylium dyes under study.

The ground state absorption spectra of benzoselenazole and benzothiazole derived dyes bearing the trifluoromethanesulfonate ($CF_3SO_3^-$) counterion, in chloroform, are presented in Fig. 2. The corresponding maximum absorption wavelengths are presented in Table 1.

The electronic absorption spectrum of the squarylium dyes under study displays a typical band, peaking between 669 and 698 nm. The changes in the UV–vis absorption spectra of the compounds studied in this paper result from the nature of the substituents in the central squaric ring. Regarding the pendent groups in R_1 position, the difference between the functionalization with ethyl or hexyl results in a very small bathochromic shift of about 2 nm and thus, Fig. 2 only presents the ethyl pendent group. The absorption wavelength will be highly dependent of the amino group substituents, accordingly with their electron-donating ability.

By comparing the three types of substituents, one can observe that the squaraines with diethylamino (**3a**, **3c**) and dihydroxyethylamino (**5a**, **5c**) groups absorb approximately at the same wavelength, while the ones that possess the hydroxyethylamino group (**4a**, **4c**) present a hypsochromic shift, when compared with the previous ones. This effect is mainly due to the number of alkyl groups, in this case, ethyl groups, incorporated in the substituent. Since alkyl groups are electron donating by induction, they can stabilize the positive charge of the amine from the substituent in the central squaric ring. In that case, the substituents with two ethyl groups (diethylamino and dihydroxyethylamino) will better stabilize that positive charge, promoting an increase of the system's resonance, shifting the absorption to higher wavelengths, when compared with hydroxyethylamino. This effect is accomplished by the electron-transfer process that occurs in the central squaric ring, from the amine to the oxygen, and that offers the system another charge delocalization pathway.

Parallel to the effect of the alkyl groups in the substituent, we also have the $-OH$ groups, which can be considered electron

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