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The synthesis and characterization of novel, aza-substituted squarylium cyanine dyes

L.V. Reis [a], J.P. Serrano [a], Paulo Almeida [b], P.F. Santos [a,*]

[a] Departamento de Química and Centro de Química – Vila Real, Universidade de Trás-os-Montes e Alto Douro, Apartado 1013, 5001-801 Vila Real, Portugal
[b] Departamento de Química and Unidade de I&D de Materiais Têxteis e Papeleiros, Universidade da Beira Interior, 6201-001 Covilhã, Portugal

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ABSTRACT

Several squarylium cyanine dyes derived from benzothiazole, benzoselenazole and quinoline were synthesised and the central four member ring functionalized by substitution of one of the oxygen atoms by benzylamine, aniline, 3-iodoaniline, *N*,*N*-dimethylhydrazine and 2-aminosulfonic acid groups. All of the ensuing, novel aza-substituted dyes displayed strong absorption within the range 651–709 nm.

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1. Introduction

Squarylium dyes are 1,3-disubstituted derivatives of squaric acid (3,4-dihydroxy-1,2-dioxocyclobut-3-ene) whose synthesis was first reported about 40 years ago [1]. Since then, they have been gaining increasing technological usefulness due to their unique properties, namely, photochemical stability, high photoconductivity and sharp and intense absorption in the red and near-infrared (NIR) regions [2]. Particularly in the last two decades, squarylium dyes have found extensive application in the domain of photonics, mainly as substrates for optical recording media [3], xerographic photoreceptors [4] and organic solar cells [5,6]. Lately, there is an emerging interest in this class of dyes as sensors for determination of metals [7–9], sensitizers for Photodynamic Therapy (PDT) [10–12] and noncovalent labels for biomolecules [13–15].

As a consequence of the continuously expanding range of applications as functional materials, the structural variation of squarylium dyes has become an active area of research. Notwithstanding, amongst the large family of compounds hitherto synthesised, those of the cyanine type have holding comparatively much less attention. Especially in what concerns the development of new sensitizers for PDT, cationic squarylium cyanine dyes are of great interest once cationic cyanines started to be regarded as promising sensitizing agents [16,17].

The structural modification of squarylium cyanines has been concentrated chiefly on the variation of the ending groups of the polymethinic chain. The functionalization of the squaric ring, on the other hand, has been considerably less explored, most of the approaches having been performed via derivatization of an intermediate monosubstituted monoalkylsquarate ester [18–21]. We have recently reported the synthesis of several new amino-squarylium cyanine dyes by an expeditious methodology involving the methylation of one of the central oxygen atoms with methyl triflate, followed by the nucleophilic substitution of the so formed methoxy group by an aliphatic amine [22].

Following our interest in the development of new potential sensitizers for PDT [23–25], we now have synthesised several new representative squarylium cyanine dyes bearing benzylamino, anilino, 3-iodoanilino, *N*,*N*-dimethylhydrazo and 2-aminoethylsulfonic groups at the central four member ring.

This functionalization of the squaric ring is thought to increase structural complexity and, inherently, the diversity of possible intermolecular interactions which may conveniently influence the solubility of the dye and its interaction with cellular components. The possible increase of intramolecular hydrogen bonding may induce additional rigidification of the dye and, therefore, a decrease of the non-radiative decay by photoisomerization and a rise of the efficiency of the dye's singlet-to-triplet interconversion. The latter is directly related to the ability of the dye to generate singlet oxygen, commonly accepted as the primary agent responsible for cell photodamage [26]. Moreover, the substitution with arylamines

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[*] Corresponding author.
E-mail address: psantos@utad.pt (P.F. Santos).

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also constitutes a straightforward way of incorporating heavy halogen atoms into the compound, which potentially enhances the singlet oxygen generation efficiency of the dye, through the internal heavy atom effect.

All the aza-substituted dyes display strong absorption within the phototherapeutic window (600–1000 nm), which is one of the basic multidisciplinary requirements for any potential candidate as sensitizer for PDT [27].

2. Results and discussion

The synthesis of the starting squarylium dyes **3a**–**c** was carried out by condensation of squaric acid and 2 molar equivalents of the appropriate *N*-hexylbenzoazolium iodide **2**, prepared through alkylation of the corresponding benzoazole **1** with 1-iodohexane, in a refluxing mixture of *n*-BuOH/pyridine. Methylation of dyes **3** with methyl triflate, in dry dichloromethane, yielded the requisite *O*-methyl ethers **4** in good yields, from which the different derivatives **5**–**9** could be easily achieved by nucleophilic substitution (Scheme 1).

Benzylamine, *N*,*N*-dimethylhydrazine and 2-aminoethylsulfonic acid reacted smoothly with *O*-methyl derivatives **4** to furnish the corresponding aza-substituted squarylium cyanines **5**, **8** and **9**, respectively, in moderate to good yields. Similar reaction with the weaker nucleophiles aniline and 3-iodoaniline to give compounds **6a** and **7a** shown previously [25] to require catalysis with a combination of triethylamine and 4-(*N*,*N*-dimethylamino)pyridine (4-DMAP) or triethylamine and 4-pyrrolidinopyridine, respectively. Compounds **6b**,**c** and **7b**,**c** were then synthesised as they benzothiazole analogues.

Each of the final substituted squarylium dyes **5**–**8** underwent counter-ion exchange upon treatment with 14% aqueous KI. The replacement of the triflate ion by iodide, apart from facilitating crystallization, is also intentioned to take advantage of the so-called external heavy atom effect and potentially enhance the dye's efficiency to convert ground-state triplet oxygen to cytotoxic singlet oxygen.

Dyes **9** apparently exist in the zwitterionic form, as suggested by the absence of the peak of the sulfonic acid labile proton in the NMR spectrum. They were, in general, less soluble in common organic solvents than the remaining substituted squarylium compounds **5**–**8**. For that reason, although the assumed selenium analogue of **9a** could be obtained as a deep-blue solid, displaying UV/vis, IR and HRFABMS spectra consistent with the proposed structure, we were unable to achieve a suitable NMR spectrum even in polar solvents such as DMSO-d_6 or MeOD.

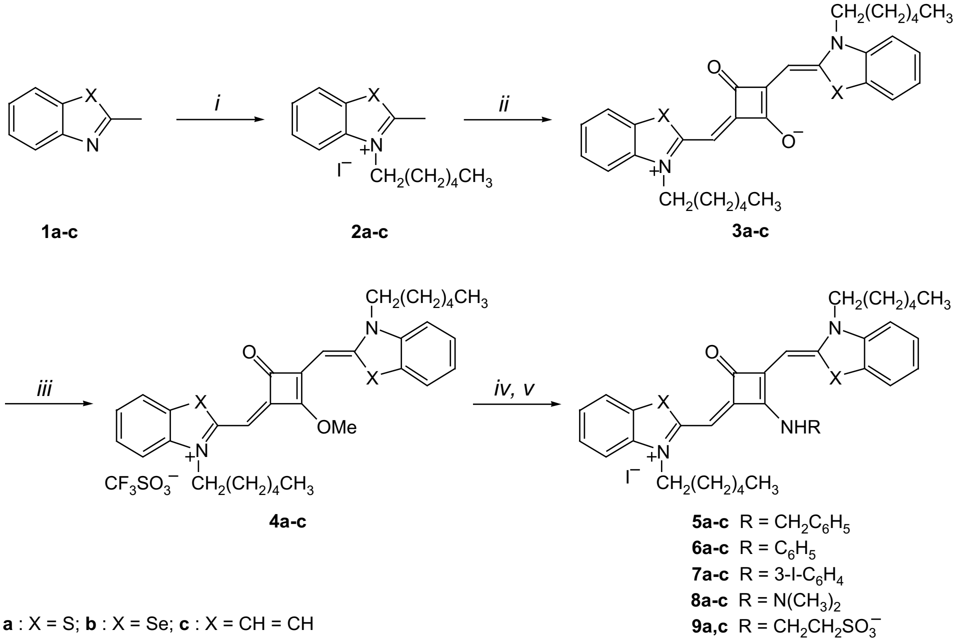
The nonexistence of counter-ion triflate in dyes **5**–**9** was promptly confirmed by the absence of both the characteristic S=O band and the downfield CF_3 signal in their IR and ^{13}C NMR spectra, respectively.

All the synthesised squarylium dyes **3**–**9** displayed sharp and intense absorption ($\varepsilon > 10^5\ cm^{-1}\ M^{-1}$) in the red end of the visible region (λ_{max} 651–709 nm) (Table 1). For each group of parent dyes the wavelength of maximum absorption rises in the order benzothiazole < benzoselenazole < quinoline, as a consequence of the higher electronegativity of sulphur in relation to selenium, and, in the case of the quinoline nucleus, of the extension of the π-conjugated system.

In general, the aza-substituted dyes derived from benzothiazole and benzoselenazole display absorption at longer wavelengths than their non-substituted analogues **3a** and **3b**. On the contrary, all the dyes based on quinoline exhibited λ_{max} inferior to that of **3c**. Higher steric hindrance, with consequent loss of planarity and diminishing orbital overlapping in more or less extent, could be the main reason for it.

The chromophore shows typical donor–acceptor characteristics with increasing bathochromic shift (or diminishing hypsochromic shift) as the electron donating properties of the auxochrome increases. Consistently, the λ_{max} of azo dyes possessing the 3-iodoanilino group, the less electron withdrawing auxochrome, is invariably blue-shifted, whatever the terminal nuclei of the dye.

Some *N*-alkylaminosquarylium dyes derived from 3,3-dimethylindolenine were referred to show sensible differences in comparison to their neutral precursors, namely, lower molar extinction coefficients and a C=O stretching band around



Scheme 1. Reagents and conditions. (i) $ICH_2(CH_2)_4CH_3$, MeCN, reflux; (ii) squaric acid, *n*-BuOH/pyridine, reflux; (iii) $CF_3SO_3CH_3$, CH_2Cl_2, N_2, r.t.; (iv) **5** and **8**: $C_6H_5CH_2NH_2$ or Me_2NHNH_2, CH_2Cl_2, N_2, r.t.; **6**: $C_6H_5NH_2$, Et_3N, 4-DMAP, CH_2Cl_2, N_2, r.t.; **7**: 3-I-$C_6H_4NH_2$, 4-pyrrolidinopyridine, CH_2Cl_2, N_2, reflux; **9**: $H_2NCH_2CH_2SO_3H$, Et_3N, CH_2Cl_2, N_2, r.t.; (v) **5**–**8**: 14% aq. KI, r.t.

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