

New fluorescent monomers and polymers displaying an intramolecular proton-transfer mechanism in the electronically excited state (ESIPT) Part II. Synthesis, spectroscopic characterization and solvatochromism of new benzazolylynylene derivatives

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Abstract

Eight new highly fluorescent benzazolylynylene monomers were synthesized by reaction of 2-(4'-amino-2'-hydroxyphenyl)benzazoles with two functionalized vinylyne derivatives and acryloyl chloride. The monomers were characterized by means of infrared, ¹³C and ¹H-NMR and elemental analysis. UV–vis and steady-state fluorescence in solution were also applied in order to characterize its photophysical behaviour. The benzoxazole and benzimidazole derivatives are fluorescent in the blue–purple region and the benzothiazole in the green region. The monomers presented a Stokes shift between 51 and 159 nm. A dual fluorescence ascribed to a conformational equilibrium in solution in the ground state dependent on the solvent polarity could be observed in the monomers. The radical polymerization of the monomers with methyl(methacrylate) allowed the production of eight new fluorescent polymers with good optical and thermal properties.

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1. Introduction

Excited state intramolecular proton-transfer mechanism (ESIPT) is a phototautomerization in the electronically excited state (Fig. 1) which occurs in heterocyclic molecules like 2-(2'-hydroxyphenyl)benzazoles [1–5]. ESIPT-exhibiting molecules often present a large Stokes shift. This phenomenon has widespread implications in

UV-light stabilizers [6,7], laser dyes [8], new polymeric materials [9–11] and also as fluorescent probes to labeling proteins [12].

In the ESIPT mechanism, the UV light absorption through the enol-*cis* (E_1) produce the excited enol-*cis* (E_1^*) which is quickly converted to an excited keto tautomer (K^*) by an intramolecular proton transfer, since the hydrogen becomes more acidic and the nitrogen more basic in the excited state [13]. Studies are also showing that the excited keto tautomer is more stable than the enol-*cis* by 1.5 kcal mol⁻¹ [14]. In the excited keto tautomer, the N–H and C=O groups are also bonded by an intramolecular hydrogen bond [15]. The K^* decays emitting fluorescence to a keto tautomer (K) and the initial enol-*cis* form is regenerated without any photochemical change [16,17].

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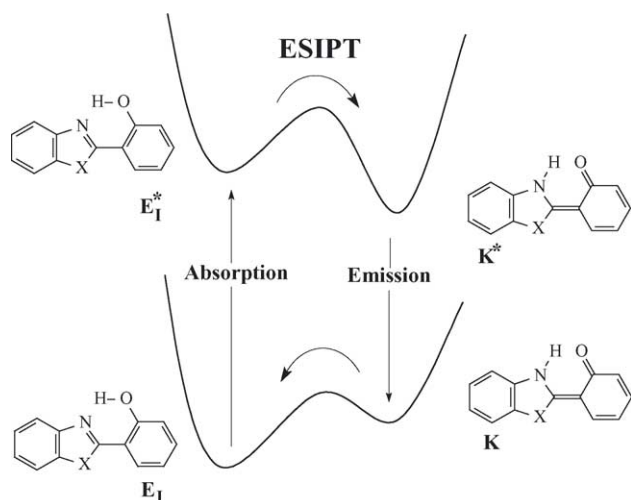
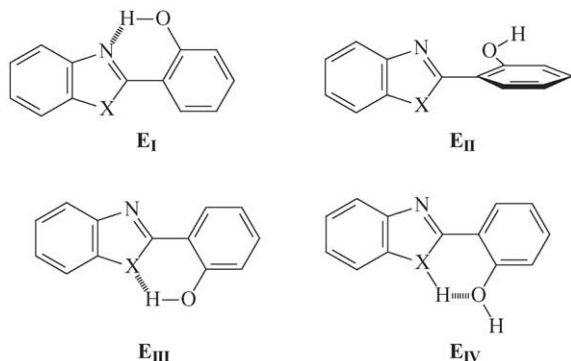


Fig. 1. ES IPT mechanism.

The ES IPT mechanism is quite dependent on the solvent polarity [18–20]. Many studies regarding this dependence, [20–24] as well as theoretical calculations involving the geometry of the conformers in solution [25–30] have been made. In protic and/or polar solvents, the enol-*cis* open conformer (E_{II}) can be stabilized by intermolecular hydrogen bond with the solvent [31]. This conformer is originated from the intramolecular hydrogen bond rupture between the hydrogen of the hydroxy group and the nitrogen in the 3-position followed by 180° rotation of the 2-hydroxyphenyl group under the C_2-C_1 , bond. In non-polar solvents additional enol-*trans* (E_{III}) conformers in benzoxazoles and benzimidazoles ($X=O$ and S , respectively) and enol-*trans* open (E_{IV}) in benzimidazoles ($X=NH$) could also exist (Scheme 1). All these conformers ($E_{II}-E_{IV}$) which present normal relaxation can compete with the keto tautomer responsible to the ES IPT mechanism [32].

Recently, we described new fluorescent MMA—benzazole dyes copolymers with good optical and thermal properties, as previously observed in similar materials [9]. In order to prepare new fluorescent polymers for optical applications, it was presented in this work the synthesis and



Scheme 1.

characterization of eight new benzazolylvinylene derivatives. A study of the solvent polarity dependence on the absorption and fluorescence emission spectra of the monomers and its radical polymerization with MMA were also performed.

2. Experimental

2.1. Materials

Reagent grade *o*-aminophenol, 1,2-phenylenediamine, *o*-aminothiophenol and 4-aminosalicylic acid (Aldrich) were used without purification. Polyphosphoric acid (PPA) was purchased from ACROS Chemicals. The vinylene derivatives were prepared according to the methodology previously described on the literature [33,34] or purchased from ACROS Chemicals. Silicagel 60 (Merck) was used for chromatographic column separations. All the solvents were used as received or purified using standard procedures [35]. The methyl(methacrylate) used in the polymerizations were purchased from Aldrich and AIBN from Merck. Spectroscopic grade solvents (Merck) were used for fluorescence and UV–vis measurements.

2.2. Methods and instruments

Infrared spectra were recorded on a Mattson Galaxy Series FT-IR3000 model 3020 in Nujol mulls. Melting points were measured with a Thermolyne apparatus and are uncorrected. 1H and ^{13}C NMR spectra were performed on a VARIAN model VXR-200 or INOVA-300 using tetramethylsilane (TMS) as the internal standard and DMSO- d_6 (Aldrich) or $CDCl_3$ (Merck) as the solvent at room temperature. UV–vis absorption spectra were performed on a Varian Cary 50 spectrophotometer. UV–vis absorption data for fluorescence quantum yield were taken on a Shimadzu UV-1601PC spectrophotometer. Fluorescence spectra were measured with a Hitachi spectrofluorometer model F-4500. Spectrum correction was performed to enable measuring a true spectrum by eliminating instrumental response such as wavelength characteristics of the monochromator or detector using Rhodamine B as a standard (quantum counter). Elemental analyses were performed by Perkin–Elmer model 240. The quantum yield of fluorescence (ϕ_f) was made at $25^\circ C$ in spectroscopic grade solvents with a solution with absorbance intensity lower than 0.05. Quinine sulphate (Riedel) in H_2SO_4 1 M ($\phi_f = 0.55$) was used as quantum yield standard [36,37]. Keto and enol quantum yields were obtained by spectral deconvolution (Microcal™ Origin® v6.0).

DSC analyses were performed with a Perkin–Elmer DSC-4 in a temperature range of $50-180^\circ C$. Dry samples, 5–7 mg, were prepared in aluminium pan and sealed. The thermograms were obtained at a rate of $10^\circ C\ min^{-1}$ with a nitrogen purge. TGA analyses were conducted with a Perkin–Elmer TGS-2 thermal gravimetric analyzer. Dry

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