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Journal of Photochemistry and Photobiology A: Chemistry 173 (2005) 81–92
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

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 benzazolylvinylene derivatives

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Received 23 August 2004; received in revised form 10 December 2004; accepted 10 January 2005
Available online 3 February 2005

Abstract

Eight new highly fluorescent benzazolylvinylene monomers were synthesized by reaction of 2-(4′-amino-2′-hydroxyphenyl)benzazoles with two functionalized vinylene derivatives and acryloyl chloride. The monomers were characterized by means of infrared, ^{13}C and ^{1}H-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.

Keywords: ESIPT; Fluorescent polymers; Benzazolylvinylene derivatives; Solvent effect

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_I) produce the excited enol-*cis* (E_I^*) 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 excite sate [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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doi:10.1016/j.jphotochem.2005.01.006

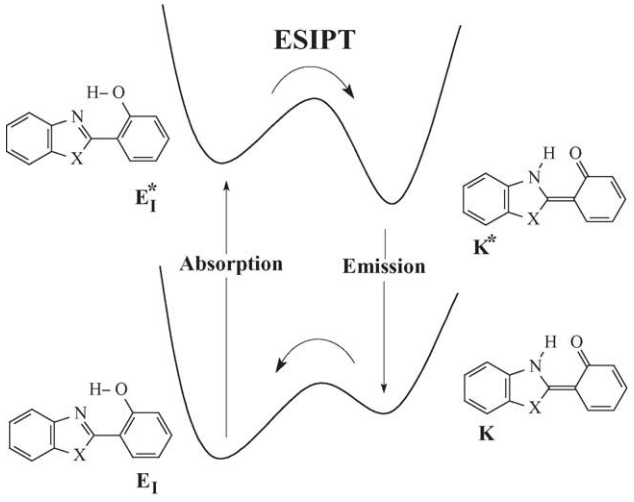
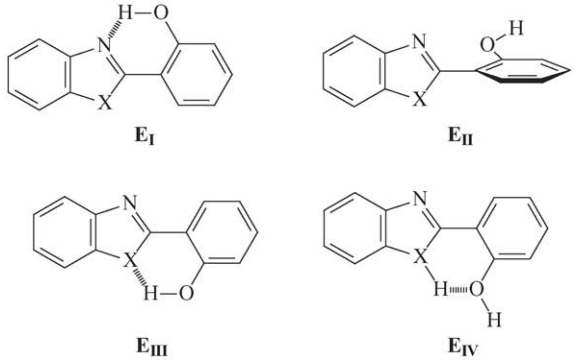


Fig. 1. ESIPT mechanism.

The ESIPT 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 ESIPT 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 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.



Scheme 1.

2. Experimental

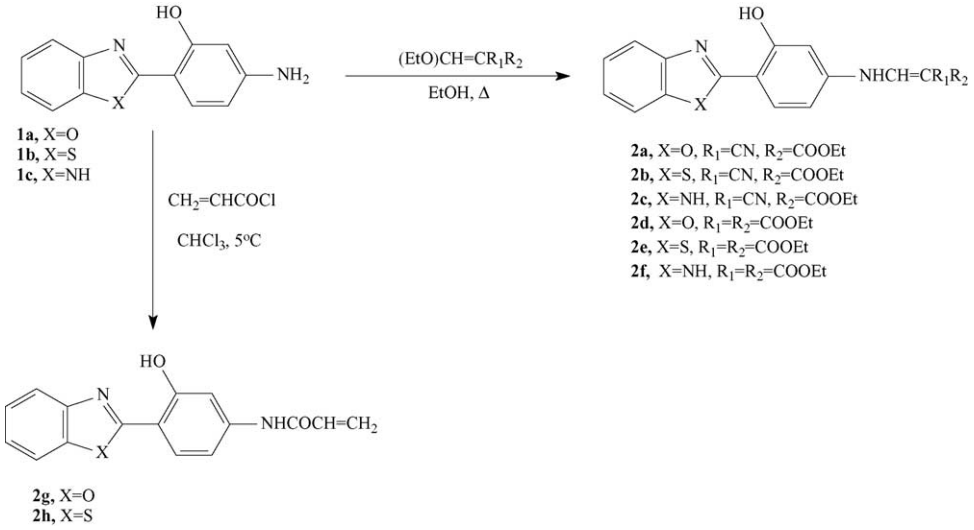
2.1. Materials

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. ^{1}H 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_{fl}) was made at 25 °C in spectroscopic grade solvents with a solution with absorbance intensity lower than 0.05. Quinine sulphate (Riedel) in H_2SO_4 1 M ($\phi_{fl} = 0.55$) 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 °C. Dry samples, 5–7 mg, were prepared in aluminium pan and sealed. The thermograms were obtained at a rate of 10 °C min^{-1} with a nitrogen purge. TGA analyses were conducted with a Perkin–Elmer TGS-2 thermal gravimetric analyzer. Dry



Scheme 2.

samples, 3–4 mg, were directly weighed into aluminium pans. A heating rate of 30 °C min^{-1} was maintained from 50 to 600 °C. Gel Permeation Chromatography (GPC) with a LDC Analytical Model Constametric 3200. Standard polystyrene was used as reference.

2.3. Synthesis and characterization

2.3.1. General procedure for the synthesis of monomer dyes

The dyes **1a–c** were obtained using a methodology previously described [38]. The benzazolylvinylene derivatives **2a–f** were prepared according Scheme 2 [9]. To a solution of 0.50 g of the corresponding **1a–c** in ethanol (40 ml) was added an equimolar amount of the vinylene derivative and heated at reflux from 24 h. The product which precipitates in the reactional mixture was filtered and dried at room temperature. The purification was made by column chromatography eluted with dichloromethane.

Another vinylene derivatives—bis(methylthio)methylene malononitrile and bis(methylthio) methylene methylcyanoacetate—were also used in the same reaction with the 2-(4′-amino-2′-hydroxyphenyl) benzazoles. After 72 h at reflux, no reaction products could be detected.

The *N*-acryloylamide derivatives **2g** and **h** were prepared using a methodology presented in Scheme 2. To a solution of 0.50 g of the corresponding benzazole **1a** and **b** in chloroform (10 ml), cooled at 5 °C, was added dropwise a solution of an equimolar amount of acryloyl chloride in chloroform. After the addition, the mixture was refluxed for 24 h, cooled and the resulting precipitate was filtered, washed with chloroform, dried at room temperature and purified by column chromatography eluted with dichloromethane. After 72 h at reflux, no reaction product could be observed with the benzazole **3c** (*X*=NH) as a starting material.

*2.3.1.1. 2-(4′-Amino-2′-hydroxyphenyl)benzoxazole (**1a**).* Yield: 68%; mp: 227–228 °C (lit. [38] 227–228 °C). Anal. calcd. for $C_{13}H_{10}N_2O_2$ (226.23 g mol^{-1}): C, 69.02; H, 4.46; N, 12.38. Found: C, 68.94; H, 4.32; N, 12.40. IR (cm^{-1}): 3493 (ν_{as} NH_2), 3386 (ν_s NH_2), 3057 (ν_{arom} C–H), 1580 and 1549 (ν_{arom} C=C). ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) = 11.47 (s, 1H, OH); 7.30 (d, 1H, $H_{6'}$, J_o = 8.4 Hz); 7.62–7.52 (m, 1H, H_9 or H_6); 7.50–7.42 (m, 1H, H_9 or H_6); 7.18–7.32 (m, 2H, H_7 and H_8); 6.28 (d, 1H, $H_{3'}$, J_m = 2.2 Hz); 6.24 (dd, 1H, $H_{5'}$, J_m = 2.2 Hz and J_o = 8.4 Hz); 4.00 (broad s, 2H, NH_2). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 98 ($C_{5'}$ or $C_{3'}$), 99 ($C_{5'}$ or $C_{3'}$), 107 ($C_{1'}$), 110 (C_4 or C_7), 117 (C_4 or C_7), 124 (C_5 or C_6), 125 (C_5 or C_6), 128 ($C_{6'}$), 140 ($C_{4'}$), 148 (C_9), 155 (C_8), 160 ($C_{2'}$), 164 (C_2).

*2.3.1.2. 2-(4′-Amino-2′-hydroxyphenyl)benzothiazole (**1b**).* Yield: 70%; mp: 211–213 °C (lit. [38] 215–216 °C). Anal. calcd. for $C_{13}H_{10}N_2OS$ (242.29 g mol^{-1}): C, 64.44; H, 4.16; N, 11.56. Found: C, 64.51; H, 4.10; N, 11.46. IR (cm^{-1}): 3472 (ν_{as} NH_2), 3376 (ν_s NH_2), 3041 (ν_{arom} C–H), 1629 and 1475 (ν_{arom} C=C). ^{1}H NMR (200 MHz, DMSO-d^6): δ (ppm) = 11.80 (broad s, 1H, OH); 8.04 (dd, 1H, H_9 or H_6, J_m = 1.0 Hz and J_o = 7.6 Hz); 7.90 (dd, 1H, H_9 or H_6, J_m = 1.0 Hz and J_o = 7.6 Hz); 7.64 (d, 1H, $H_{6'}$, J_o = 8.4 Hz); 7.48 (t, 1H, H_8 or H_7, J_m = 1.0 Hz and J_o = 7.6 Hz); 7.34 (t, 1H, H_8 or H_7, J_m = 1.0 Hz and J_o = 7.6 Hz); 6.28 (dd, 1H, $H_{5'}$, J_m = 2.2 Hz and J_o = 8.4 Hz); 6.18 (d, 1H, $H_{3'}$, J_m = 2.2 Hz); 5.96 (broad s, 2H, NH_2). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ (ppm) = 102 ($C_{5'}$), 107 ($C_{3'}$), 108 ($C_{1'}$), 121 (C_4 or C_7), 122 (C_4 or C_7), 125 (C_5 or C_6), 126 (C_5 or C_6), 130 ($C_{6'}$ or $C_{4'}$), 132 ($C_{6'}$ or $C_{4'}$), 151 (C_9 or C_8), 152 (C_9 or C_8), 160 ($C_{2'}$), 170 (C_2).

*2.3.1.3. 2-(4′-Amino-2′-hydroxyphenyl)benzimidazole (**1c**).* Yield: 66%; mp: 245–247 °C (lit. [38] 241–242 °C). Anal. calcd. for $C_{13}H_{11}N_3O$ (225.25 g mol^{-1}): C, 69.32; H, 4.92;

N, 18.66. Found: C, 69.27; H, 5.22; N, 17.92. IR (cm^{-1}): 3477 (ν_{as} NH_2), 3386 (ν_s NH_2), 3217 (ν NH), 3041 (ν_{arom} C–H), 1641 (ν_{arom} C=C). ^1H NMR (300 MHz, DMSO-d^6): δ (ppm) = 13.60 (broad s, 1H, OH); 12.76 (broad s, 1H, NH); 7.70 (d, 1H, $H_{6'}$, J_o = 8.6 Hz); 7.55 (broad d, 2H, H_8 and H_7); 7.25–7.15 (m, 2H, H_9 and H_6); 6.26 (dd, 1H, $H_{5'}$, J_m = 2.0 Hz and J_o = 8.6 Hz); 6.18 (dd, 1H, $H_{3'}$, J_m = 2.0 Hz); 5.68 (broad s, 2H, NH_2). ^{13}C NMR (75.4 MHz, DMSO-d^6): δ (ppm) = 100 ($C_{1'}$ or $C_{3'}$), 101 ($C_{1'}$ or $C_{3'}$), 107 ($C_{5'}$), 111 (C_4 or C_7), 117 (C_4 or C_7), 122 (C_5 or C_6), 127 (C_5 or C_6), 133 ($C_{6'}$), 141 ($C_{4'}$), 153 (C_9 or C_8), 153 (C_9 or C_8), 153 (C_2), 160 ($C_{2'}$).

*2.3.1.4. 2-(4′-N-ethylmethylenecyanoacetate-2′-hydroxyphenyl)benzoxazole (**2a**).* Yield: 76%; mp: 258–260 °C. Anal. calcd. for $C_{19}H_{15}N_3O_4$ (349.35 g mol^{-1}): C, 65.32; H, 4.33; N, 12.03. Found: C, 65.82; H, 4.23; N, 11.98. IR (cm^{-1}): 3202 (ν NH), 3072 (ν_{arom} C–H), 2958 (ν_{alif} C–H), 2213 (ν C≡N), 1710 (ν C=O), 1679 (ν_{alif} C=C), 1618 (ν_{arom} C=C), 1587 (ν_{arom} C=C) and 1250 (ν C–O–C). ^1H NMR (300 MHz, DMSO-d^6): δ (ppm) = 11.42 (broad s, 1H, OH); 10.80 (d, 1H, NH, J = 12.9 Hz); 8.62 (d, 1H, J = 12.9 Hz); 8.04 (d, 1H, $H_{6'}$, J_o = 8.7 Hz); 7.90–7.82 (m, 2H, H_9 and H_6); 7.44–7.54 (m, 2H, H_8 and H_7); 7.18 (d, 1H, $H_{3'}$, J_m = 1.8 Hz); 7.24 (dd, 1H, $H_{5'}$, J_m = 1.8 Hz and J_o = 8.7 Hz); 4.35–4.20 (q, 2H); 1.40–1.25 (t, 3H). ^{13}C NMR (75.4 MHz, DMSO-d^6): δ (ppm) = 14 ($C_{16'}$), 62 ($C_{15'}$), 105 ($C_{5'}$ or $C_{3'}$), 105 ($C_{5'}$ or $C_{3'}$), 107 ($C_{8'}$ or $C_{1'}$), 109 ($C_{8'}$ or $C_{1'}$), 111 ($C_{10'}$), 117 (C_4 or C_7), 119 (C_4 or C_7), 125 (C_5 or C_6), 125 (C_5 or C_6), 131 ($C_{6'}$ or $C_{4'}$), 132 ($C_{6'}$ or $C_{4'}$), 139 ($C_{9'}$), 152 (C_8 or C_9), 153 (C_8 or C_9), 159 ($C_{2'}$), 164 (C_2), 167 ($C_{12'}$).

*2.3.1.5. 2-(4′-N-ethylmethylenecyanoacetate-2′-hydroxyphenyl)benzothiazole (**2b**).* Yield: 43%; mp: 229–231 °C. Anal. calcd. for $C_{19}H_{15}N_3O_3S$ (365.41 g mol^{-1}): C, 62.45; H, 4.14; N, 11.50. Found: C, 63.06; H, 4.72; N, 10.95. IR (cm^{-1}): 3376 (ν NH), 3072 (ν_{arom} C–H), 2956 (ν_{alif} C–H), 2216 (ν C≡N), 1725 (ν C=O), 1670 (ν_{alif} C=C), 1618 e 1580 (ν_{arom} C=C) and 1246 (ν C–O–C). ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 12.80 (s, 1H, OH); 10.73 (d, 1H, NH, J = 12.6 Hz); 7.88 (d, 1H, H_9 or H_6, J_o = 7.8 Hz); 7.82 (d, 1H, H_9 or H_6, J_o = 7.3 Hz); 7.80 (d, 1H, J = 13.0 Hz); 7.60 (d, 1H, $H_{6'}$, J_o = 8.5 Hz); 7.46 (t, 1H, H_8 or H_7, J_m = 1.0 Hz and J_o = 7.3 Hz); 7.36 (t, 1H, H_8 or H_7, J_m = 1.0 Hz and J_o = 7.3 Hz); 6.70 (d, 1H, $H_{3'}$, J_m = 2.4 Hz); 6.60 (dd, 1H, $H_{5'}$, J_m = 2.2 Hz and J_o = 8.5 Hz); 4.20–4.30 (q, 2H); 1.25–1.35 (t, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) = 14 ($C_{16'}$), 62 ($C_{15'}$), 105 ($C_{5'}$ or $C_{3'}$), 105 ($C_{5'}$ or $C_{3'}$), 108 ($C_{8'}$ or $C_{1'}$), 108 ($C_{8'}$ or $C_{1'}$), 114 ($C_{10'}$), 121 (C_4 or C_7), 122 (C_4 or C_7), 126 (C_5 or C_6), 127 (C_5 or C_6), 130 ($C_{6'}$ or $C_{4'}$), 132 ($C_{6'}$ or $C_{4'}$), 141 ($C_{9'}$), 151 (C_8 or C_9), 152 (C_8 or C_9), 160 ($C_{2'}$), 167 ($C_{12'}$), 168 (C_2).

*2.3.1.6. 2-(4′-N-ethylmethylenecyanoacetate-2′-hydroxyphenyl)benzimidazole (**2c**).* Yield: 78%; mp: 300–302 °C (decomp.). Anal. calcd. for $C_{19}H_{16}N_4O_3$ (348.36 g mol^{-1}): C, 65.51; H, 4.63; N, 16.08. Found: C, 65.10; H, 4.78; N, 16.30. IR (cm^{-1}): 3218 (ν NH), 3065 (ν_{arom} C–H), 2966 (ν_{alif} C–H), 2214 (ν C≡N), 1690 (ν C=O), 1610 (ν_{arom} C=C), 1634 (ν_{alif} C=C), 1587 (ν_{arom} C=C), 1244 (ν C–O–C). ^1H NMR (300 MHz, DMSO-d^6): δ (ppm) = 13.40 (broad s, 1H, OH); 13.13 (broad s, 1H, NH); 10.69 (s, 1H, NH, J = 13.8 Hz); 8.52 (d, 1H, H, J = 13.8 Hz); 8.01 (d, 1H, $H_{6'}$, J_o = 8.4 Hz); 7.76–7.50 (m, 2H, H_9 and H_6); 7.34–7.18 (m, 2H, H_8 and H_7); 7.06 (dd, 1H, $H_{5'}$, J_m = 1.8 Hz and J_o = 9.3 Hz); 7.03 (d, 1H, $H_{3'}$, J_m = 1.8 Hz); 4.30–4.10 (q, 2H); 1.35–1.20 (t, 3H). ^{13}C NMR (75.4 MHz, DMSO-d^6): δ (ppm) = 14 ($C_{16'}$), 61 ($C_{15'}$), 105 ($C_{5'}$ or $C_{3'}$), 105 ($C_{5'}$ or $C_{3'}$), 108 ($C_{8'}$ or $C_{1'}$), 109 ($C_{8'}$ or $C_{1'}$), 115 (C_4 or C_7), 118 (C_4 or C_7), 122 ($C_{10'}$), 127 (C_5 or C_6), 127 (C_5 or C_6), 141 ($C_{6'}$ or $C_{4'}$), 142 ($C_{6'}$ or $C_{4'}$), 151 (C_8 or C_9), 151 (C_8 or C_9), 153 ($C_{9'}$), 159 ($C_{2'}$), 164 (C_2), 166 ($C_{12'}$).

*2.3.1.7. 2-(4′-N-diethylmethylenemalonate-2′-hydroxyphenyl)benzoxazole (**2d**).* Yield: 89%; mp: 176–178 °C. Anal. calcd. for $C_{21}H_{20}N_2O_6$ (396.40 g mol^{-1}): C, 63.63; H, 5.09; N, 7.07. Found: C, 64.35; H, 4.92; N, 6.93. IR (cm^{-1}): 3187 (ν NH), 3050 (ν_{arom} C–H), 2988 (ν_{alif} C–H), 1740 (ν C=O), 1687 (ν_{alif} C=C), 1626 and 1543 (ν_{arom} C=C) and 1243 (ν C–O–C). ^1H NMR (200 MHz, $CDCl_3$): δ (ppm) = 11.74 (s, 1H, OH); 11.10 (d, 1H, NH, J = 13.2 Hz); 8.56 (d, 1H, J = 13.4 Hz); 8.20 (d, 1H, $H_{6'}$, J_o = 8.4 Hz); 7.80–7.68 (m, 1H, H_9 or H_6); 7.66–7.56 (m, 1H, H_9 or H_6); 7.46–7.54 (m, 2H, H_7 and H_8); 6.90 (d, 1H, $H_{3'}$, J_m = 2.2 Hz); 6.78 (dd, 1H, $H_{5'}$, J_m = 2.2 Hz and J_o = 8.6 Hz); 4.45–4.30 (q, 2H); 4.35–4.20 (q, 2H); 1.50–1.38 (t, 3H); 1.42–1.30 (t, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ (ppm) = 14 ($C_{14'}$ or $C_{19'}$), 14 ($C_{14'}$ or $C_{19'}$), 60 ($C_{13'}$ or $C_{18'}$), 61 ($C_{13'}$ or $C_{18'}$), 95 ($C_{8'}$), 104 ($C_{5'}$), 107 ($C_{1'}$ or $C_{3'}$), 109 ($C_{1'}$ or $C_{3'}$), 111 (C_4 or C_7), 119 (C_4 or C_7), 125 (C_5 or C_6), 125 (C_5 or C_6), 129 ($C_{6'}$ or $C_{4'}$), 129 ($C_{6'}$ or $C_{4'}$), 143 ($C_{9'}$), 150 (C_8 or C_9), 150 (C_8 or C_9), 160 ($C_{2'}$), 162 ($C_{10'}$ or $C_{15'}$), 165 ($C_{10'}$ or $C_{15'}$), 169 (C_2).

*2.3.1.8. 2-(4′-N-diethylmethylenemalonate-2′-hydroxyphenyl)benzothiazole (**2e**).* Yield: 46%; mp: 174–175 °C. Anal. calcd. for $C_{21}H_{20}N_2O_5S$ (412.46 g mol^{-1}): C, 61.15; H, 4.89; N, 6.79. Found: C, 61.42; H, 5.15; N, 6.58. IR (cm^{-1}): 3256 (ν NH), 2965 (ν_{alif} C–H), 1686 (ν C=O), 1647 (ν_{alif} C=C), 1608 and 1585 (ν_{arom} C=C), and 1241 (ν C–O–C). ^1H NMR (200 MHz, $CDCl_3$): δ (ppm) = 12.80 (broad s, 1H, OH); 11.03 (d, 1H, NH, J = 13.4 Hz); 8.52 (d, 1H, J = 13.4 Hz); 7.96 (d, 1H, H_9 or H_6, J_o = 7.4 Hz); 7.88 (d, 1H, H_9 or H_6, J_o = 7.2 Hz); 7.64 (d, 1H, $H_{6'}$, J_o = 8.4 Hz); 7.50 (t, 1H, H_8 or H_7, J_m = 0.8 Hz and J_o = 7.3 Hz); 7.28 (t, 1H, H_8 or H_7, J_m = 0.8 Hz and J_o = 7.3 Hz); 6.84 (d, $H_{3'}$, J_m = 2.0 Hz); 6.68 (dd, 1H, $H_{5'}$, J_m = 2.0 Hz and J_o = 8.6 Hz); 4.35–4.20 (q, 2H); 4.27–4.45 (q, 2H); 1.50–1.36 (t, 3H); 1.40–1.30 (t, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ (ppm) = 14 ($C_{14'}$ or $C_{19'}$), 14 ($C_{14'}$ or $C_{19'}$), 60 ($C_{13'}$ or $C_{18'}$), 60 ($C_{13'}$ or $C_{18'}$), 95 ($C_{8'}$), 104

($C_{1'}$), 109 ($C_{3'}$), 113 ($C_{5'}$), 121 (C_4 or C_7), 121 (C_4 or C_7), 125 (C_5 or C_6), 127 (C_5 or C_6), 130 ($C_{6'}$ or $C_{4'}$), 132 ($C_{6'}$ or $C_{4'}$), 142 ($C_{9'}$), 150 (C_8 or C_9), 152 (C_8 or C_9), 159 ($C_{2'}$), 165 (C_2), 168 ($C_{10'}$ or $C_{15'}$), 169 ($C_{10'}$ or $C_{15'}$).

*2.3.1.9. 2-(4′-N-diethylmethylenemalonate-2′-hydroxyphenyl)benzimidazole **(2f)***. Yield: 81%; mp: 228–230 °C. Anal. calcd. for $C_{21}H_{21}N_3O_5$ (395.41 g mol^{-1}): C, 63.79; H, 5.35; N, 10.63. Found: C, 63.83; H, 5.36; N, 10.20. IR (cm^{-1}, Nujol): 3202 (ν NH), 3065 (ν_{arom} C–H), 2960 (ν_{alif} C–H), 1690 (ν C=O), 1657 (ν_{alif} C=C), 1626 and 1587 (ν_{arom} C=C) and 1236 (ν C–O–C). ^{1}H NMR (200 MHz, DMSO-d^6): δ (ppm) = 13.40 (broad s, 1H, OH); 13.25 (broad s, 1H, NH); 10.70 (s, 1H, NH, J = 13.8 Hz); 8.44 (d, 1H, H, J = 13.8 Hz); 8.05 (d, 1H, $H_{6'}$, J_o = 9.2 Hz); 7.70–7.58 (m, 2H, H_9 and H_6); 7.34–7.20 (m, 2H, H_8 and H_7); 7.06 (dd, 1H, $H_{5'}$, J_m = 1.0 Hz and J_o = 9.2 Hz); 7.04 (d, 1H, $H_{3'}$, J_m = 1.0 Hz); 4.30–4.18 (q, 2H); 4.22–4.05 (q, 2H); 1.31–1.27 (t, 3H); 1.32–1.28 (t, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) = 14 ($C_{14'}$ or $C_{19'}$), 14 ($C_{14'}$ or $C_{19'}$), 60 ($C_{13'}$ or $C_{18'}$), 60 ($C_{13'}$ or $C_{18'}$), 94 ($C_{8'}$), 104 ($C_{3'}$ or $C_{5'}$), 105 ($C_{3'}$ or $C_{5'}$), 109 ($C_{1'}$), 108 (C_4 or C_7), 108 (C_4 or C_7), 122 (C_5 or C_6), 122 (C_5 or C_6), 127 ($C_{6'}$ or $C_{4'}$), 127 ($C_{6'}$ or $C_{4'}$), 142 ($C_{9'}$), 149 (C_8 or C_9), 151 (C_8 or C_9), 159 ($C_{2'}$), 160 ($C_{10'}$ or $C_{15'}$), 164 ($C_{10'}$ or $C_{15'}$), 167 (C_2).

*2.3.1.10. 2-(4′-N-acryloylamide-2′-hydroxyphenyl)benzoxazole **(2g)***. Yield: 44%; mp: 255–257 °C. Anal. calcd. for $C_{16}H_{12}N_2O_3$ (280.28 g mol^{-1}): C, 68.56; H, 4.32; N, 9.99. Found: C, 68.03; H, 4.12; N, 10.15. IR (cm^{-1}): 3102 (ν NH), 3041 (ν_{arom} C–H), 2958 (ν_{alif} C–H), 1702 (ν C=O), 1618 (ν_{alif} C=C), 1580 and 1542 (ν_{arom} C=C). ^{1}H NMR (200 MHz, DMSO-d^6): δ (ppm) = 11.26 (s, 1H, OH); 10.47 (s, 1H, NH); 8.00 (d, 1H, $H_{6'}$, J_o = 8.6 Hz); 7.90–7.85 (m, 2H, H_9 and H_6 or H_7 and H_8) 7.15 (d, 1H, $H_{3'}$, J_m = 1.8 Hz); 7.40–7.50 (m, 2H, H_7 and H_8 or H_9 and H_6); 7.35 (dd, 1H, $H_{5'}$, J_m = 1.8 Hz and J_o = 8.6 Hz); 6.50 (dd, 1H, H_X, J_{trans} = 17 Hz and J_{cis} = 9.8 Hz); 6.35 (dd, 1H, H_A, J_{trans} = 17 Hz and J_{gem} = 2.4 Hz); 5.85 (dd, 1H, H_B, J_{cis} = 9.8 Hz and J_{gem} = 2.4 Hz). ^{13}C NMR (75.4 MHz, DMSO-d^6): δ (ppm) = 105 ($C_{1'}$ or $C_{10'}$), 106 ($C_{1'}$ or $C_{10'}$), 110 ($C_{3'}$ or $C_{5'}$), 111 ($C_{3'}$ or $C_{5'}$), 118 ($C_{6'}$), 125 (C_4 or C_7), 125 (C_4 or C_7), 128 (C_5 or C_6), 128 (C_5 or C_6), 131 ($C_{4'}$), 139 (C_8 or C_9), 143 (C_8 or C_9), 148 ($C_{11'}$), 158 ($C_{2'}$), 162 ($C_{8'}$ or C_2), 163 ($C_{8'}$ or C_2).

*2.3.1.11. 2-(4′-N-acryloylamide-2′-hydroxyphenyl)benzothiazole **(2h)***. Yield: 39%; mp: 241–243 °C. Anal. calcd. for $C_{16}H_{12}N_2O_2S$ (296.34 g mol^{-1}): C, 64.85; H, 4.08; N, 9.45. Found: C, 64.85; H, 4.18; N, 8.97. IR (cm^{-1}): 3569 (ν NH), 2959 (ν_{alif} C–H), 1679 (ν C=O), 1630 (ν_{alif} C=C), 1607 and 1555 (ν_{arom} C=C). ^{1}H NMR (200 MHz, DMSO-d^6): δ (ppm) = 11.70 (broad s, 1H, OH); 10.40 (s, 1H, NH); 8.15 (d, 1H, $H_{6'}$, J_o = 8.6 Hz); 8.11 (d, 1H, H_9 or H_6, J_o = 7.0 Hz); 8.02 (d, 1H, H_9 or H_6, J_o = 7.0 Hz); 7.70 (d, 1H, $H_{3'}$, J_m = 1.2 Hz); 7.52 (t, 1H, H_8 or H_7, J_o = 7.6 Hz); 7.42 (t, 1H, H_8 or H_7, J_o = 7.6 Hz); 7.24 (dd, 1H, $H_{5'}$, J_m = 1.2 Hz and J_o = 8.6 Hz); 6.50 (dd, 1H, H_X, J_{trans} = 17 Hz and J_{cis} = 9.6 Hz); 6.30 (dd, 1H, H_A, J_{trans} = 16.8 Hz and J_{gem} = 2.2 Hz); 5.82 (dd, 1H, H_B, J_{cis} = 9.6 Hz and J_{gem} = 2.2 Hz). ^{13}C NMR (50 MHz, DMSO-d^6): δ (ppm) = 106 ($C_{10'}$), 111 ($C_{3'}$ or $C_{5'}$), 113 ($C_{3'}$ or $C_{5'}$), 122 (C_4 or C_7), 122 (C_4 or C_7), 124 ($C_{1'}$), 126 (C_5 or C_6), 127 (C_5 or C_6), 129 ($C_{6'}$ or $C_{4'}$), 131 (C_6 or $C_{4'}$), 134 (C_8 or C_9), 142 (C_8 or C_9), 151 ($C_{11'}$), 157 ($C_{2'}$), 164 ($C_{8'}$ or C_2), 165 ($C_{8'}$ or C_2).

2.3.2. Polymer synthesis

The copolymers **2a–h** were prepared by heating a solution of the benzazole dyes (~10^{-3} M) in MMA (4 ml), which was purified before polymerization passing on an activated alumina column. 2,2′-Azoisobutyronitrile (AIBN) (12 mg), purified before use by recrystallization from methanol and maintained under vacuum, was used as initiator for the polymerization. The initial temperature was 40 °C for 2 days and then increased up to 60 °C. After 6 days, the samples were heated for 2 h at 70 °C and subsequently the temperature remained at 80 °C for 8 h as previously described [9]. During the polymerization, the temperature was maintained with an accuracy of ±0.5 °C. The copolymers were purified by solubilization in chloroform and precipitation into cyclohexane (1:20 ml solvent/non-solvent). The resulting fluorescent copolymers are presented in Scheme 3.

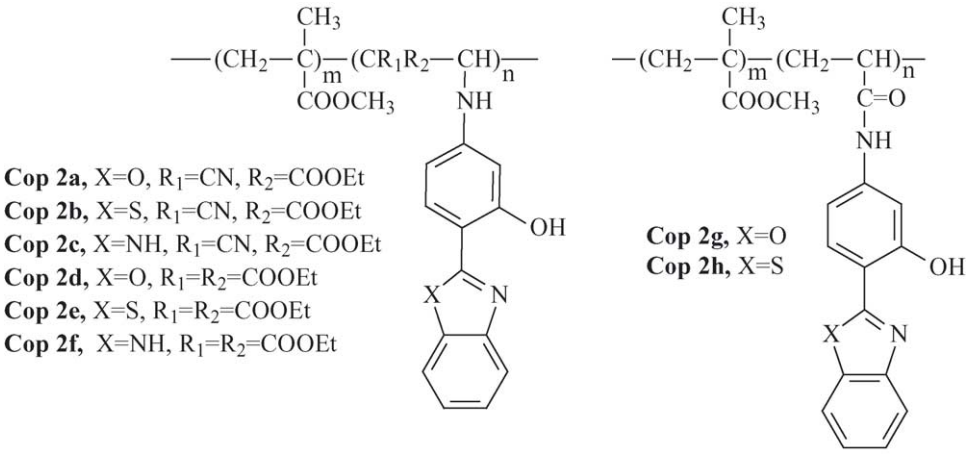
3. Results and discussion

3.1. UV–vis and fluorescence characterization of monomer dyes

The UV–vis absorption and fluorescence emission spectra were made in seven different solvents: acetonitrile, benzene, dioxane, dichloromethane, ethyl acetate, ethanol and methanol. All experiments were performed at room temperature in a concentration of 10^{-6} M. The UV–vis absorption and fluorescence emission spectra are normalized.

As it can be seen in Fig. 2, the monomers **2a** and **c** present an absorption maximum (λ_{max}^{abs}) located around 360 nm whereas **2b** appear around 370 nm with molar extinction coefficients ε values (10^4 l mol^{-1} cm^{-1}) in agreement with π–π^* transitions. The absorption maximum present a smooth dependence (~10 nm) on the solvent polarity, and shows a blue shift with increasing the solvent polarity (Table 1) as already observed in similar heterocycles [39], probably indicating a conformational equilibrium in solution in the ground state [40,41].

The fluorescence emission spectra of the monomers **2b** and **c** show the corresponding ESIPT band around 500 nm, as expected, with a very small blue shifted band at 420 and 400 nm to **2b** and **c**, respectively. For the dye **2a**, a more intense blue shifted band can be seen, indicating the conformational equilibrium in solution in the ground state. Usually,



Scheme 3.

a dual fluorescence emission presents a band at higher wavelengths attributed to an excited keto tautomer (K^*) which arises from the enol-*cis* conformer (E_I) in the excited state, and a blue shifted one due to the conformational forms, which presents a normal relaxation [26,31] which structure depend on the solvent polarity. In this way, for the dye **2a** in aprotic and/or low polar solvents, the conformational equilibrium is probably between the E_I–E_{III} conformers which will emit fluorescence by normal relaxation. In protic solvents, it is due to the conformers E_I and E_{II}. In some cases, the relaxation in these solvents can be due to an intermolecular proton transfer with the solvent. For the dyes **2b** and **c**, a small band can be observed. The conformational equilibrium is expected to be present, probably with the enol-*cis* conformer (E_I) predominance in the ground-state. The small blue shifted band observed for the dyes **2b** and **c** is probably due to an enol-*cis* open conformer (E_{II}) for the benzothiazole and to an enol-*cis* open conformer (E_{II}) and/or enol-*trans* open (E_{IV}) for the benzimidazole. Since, even in protic and polar solvents, to the dyes **2b** and **c** the enol-*cis* conformer (E_I) is predominant in the ground state, the relative force of the intramolecular hydrogen bond in the benzimidazole **2c** and benzothiazole **2b** is higher then in benzoxazole **2a** derivative.

Table 1 shows the quantum yield of the dyes **2a–c** in different solvents. In these dyes, the quantum yield of the keto tautomer presented higher values if compared to the enol conformer, as expected. Comparing the quantum yield of fluorescence between the three keto tautomers, the dye **2a** presents the low value (≈0.02), probably due to the conformers present in the ground state which decay by normal relaxation. To the dyes **2b** and **c**, higher values were obtained (0.11 and 0.14, respectively) with a maximum observed in dichloromethane

Table 1
UV–vis and fluorescence emission data of the dyes **2a–c**

Dye	Solvent	λ_{max}^{abs} (nm)	$\varepsilon_{max} \times 10^{-4}$ (l mol^{-1} cm^{-1})	λ_{max}^{em} (nm)	$\Delta\lambda_{ST}^{keto}$ (cm^{-1})	$(\phi_{fl})_{enol}$	$(\phi_{fl})_{keto}$
2a	Acetonitrile	356	5.1	469	6768	0.0134	0.0223
	Benzene	365	5.0	470	6121	0.0166	0.0276
	Dioxane	361	5.9	470	6424	0.0250	0.0297
	Dichloromethane	358	4.8	466	6474	0.0177	0.0251
	Ethyl acetate	358	6.3	470	6656	0.0136	0.0205
	Ethanol	358	4.7	469	6611	0.0110	0.0284
	Methanol	356	5.6	469	6768	0.0155	0.0221
2b	Acetonitrile	366	5.4	500	7322	0.0086	0.1044
	Benzene	376	14.6	503	6715	0.0145	0.1229
	Dioxane	373	7.7	503	6929	0.0254	0.0653
	Dichloromethane	369	8.6	497	6979	0.0043	0.3175
	Ethyl acetate	368	15.3	503	7293	0.0029	0.0403
	Ethanol	369	5.3	500	7100	0.0109	0.0995
	Methanol	366	5.1	499	7282	0.0098	0.0597
2c	Acetonitrile	357	8.4	492	7686	0.0078	0.0965
	Benzene	366	13.0	469	6000	0.0048	0.2045
	Dioxane	360	10.0	469	6456	0.0093	0.1861
	Dichloromethane	364	4.5	470	6196	0.0098	0.3365
	Ethyl acetate	359	6.0	475	6802	0.0037	0.1181
	Ethanol	359	17.9	487	7321	0.0029	0.0215
	Methanol	357	13.2	487	7477	0.0075	0.0113

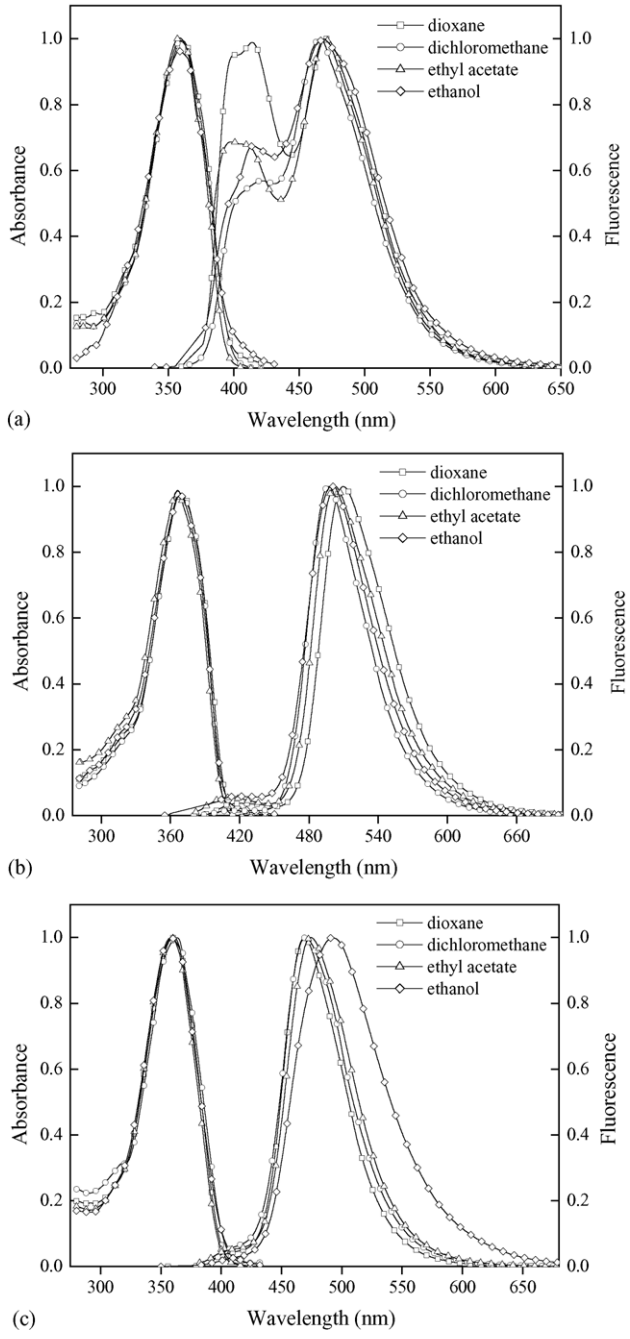


Fig. 2. Normalized absorption and fluorescence emission spectra of **2a–c**.

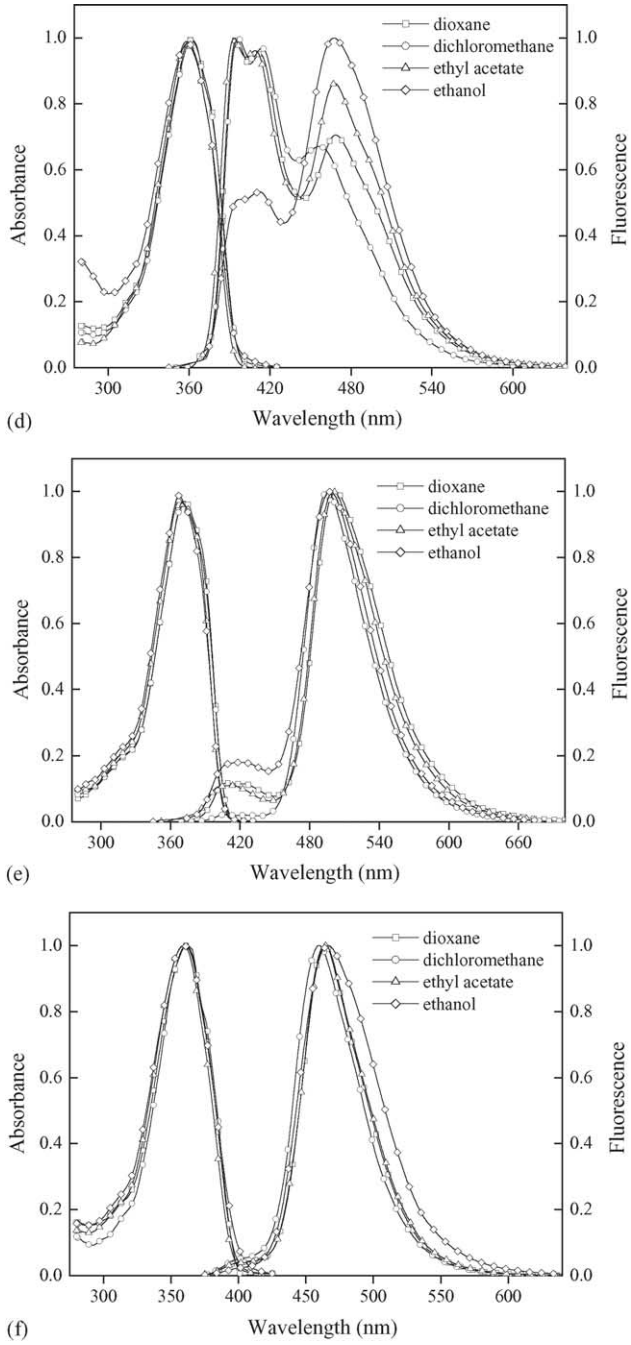


Fig. 3. Normalized absorption and fluorescence emission spectra of **2d–f**.

(**2b**: 0.3175 and **2c**: 0.3365). Since the ESIPT mechanism is quite dependent on the solvent polarity, this variation on the quantum yield of fluorescence was expected.

To the dyes **2d–f**, a conformational equilibrium in solution in the ground state is also expected to be present since their show a shift of 8–11 nm in the absorption maximum (Fig. 3). The benzazole and benzimidazole derivatives (**2d** and **f**) presented λ_{max}^{abs} around 360 nm and the benzothiazole (**2e**) around 370 nm with molar extinction coefficients ($10^4\,l\,mol^{-1}\,cm^{-1}$) in agreement with π–π^* transitions (Table 2). In the fluorescence emission spectra, a dual fluorescence emission can be seen in the benzoxazole derivative **2d** as already observed to the monomer **2a**. To this dye, the ESIPT band is located at 470 nm. In aprotic and low polar solvents, the same E_I–E_{III} conformers are expected to be present to **2d** in the ground state, and in protic and polar solvents the conformers E_I and E_{II} could be present. The *m*-orientated group to the hydroxy group also affects the intramolecular hydrogen bond in these derivatives.

The fluorescence emission of the benzothiazole and benzimidazole derivatives **2e** and **f** present a main emission band located around 500 and 475 nm with a small blue shifted band

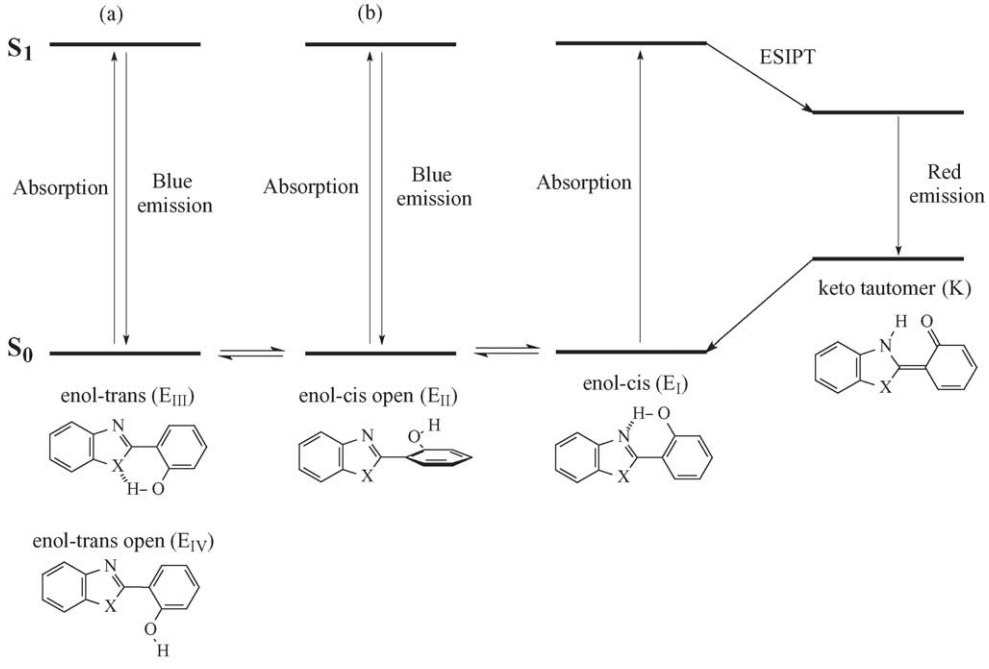
Table 2
UV–vis and fluorescence emission data of the dyes **2d–f**

Dye	Solvent	λ_{max}^{abs} (nm)	$\varepsilon_{max} \times 10^{-4}$ (l mol^{-1} cm^{-1})	λ_{max}^{em} (nm)	$\Delta\lambda_{ST}^{keto}$ (cm^{-1})	$(\phi_{fl})_{enol}$	$(\phi_{fl})_{keto}$
2d	Acetonitrile	357	3.9	466	6552	0.0671	0.0865
	Benzene	364	4.0	415	3376	0.0552	0.1523
	Dioxane	361	5.5	469	6378	0.1331	0.1317
	Dichloromethane	362	3.1	457	5742	0.1092	0.0992
	Ethyl acetate	358	6.8	468	6565	0.0574	0.0544
	Ethanol	359	4.5	466	6396	0.0366	0.0744
	Methanol	355	5.5	466	6710	0.0212	0.0507
2e	Acetonitrile	366	5.3	497	7202	0.0154	0.0976
	Benzene	375	9.9	501	6707	0.0156	0.1567
	Dioxane	372	8.3	502	6961	0.0100	0.0762
	Dichloromethane	372	7.6	495	6680	0.0105	0.2066
	Ethyl acetate	368	13.8	501	7214	0.0137	0.0326
	Ethanol	368	21.5	498	7093	0.0190	0.1121
	Methanol	367	6.3	497	7127	0.0078	0.0422
2f	Acetonitrile	358	8.4	467	6520	0.0113	0.2394
	Benzene	364	13.0	464	5921	0.0076	0.3885
	Dioxane	361	10.0	464	6149	0.0129	0.4240
	Dichloromethane	362	4.5	466	6165	0.0137	0.3710
	Ethyl acetate	359	6.0	464	6303	0.0084	0.2981
	Ethanol	360	17.9	465	6272	0.0049	0.1701
	Methanol	353	13.2	465	6823	0.0079	0.0667

at 420 and 400 nm, respectively. The conformational equilibrium is expected to be present, probably with the enol-*cis* conformer (E_I) predominance in the ground state, as observed to the dye **2a**. The difference of intensities of the blue shifted bands can be an indicative between the relative forces of the intramolecular hydrogen bond of this dye family with benzimidazole > benzothiazole > benzoxazole.

Higher values of the quantum yields of the dyes **2d–f** could be obtained if compared to dyes **2a–c**. As previously observed for **2a–c**, the keto tautomers presented higher values if compared to the enol conformers and the oxazole derivative **2d** present the low values (≈0.09) when compared to the imidazole (≈0.103) and the thiazole (≈0.279) analogues.

The photophysical study on the *N*-vinylene derivatives **2a–f** showed that the oxazolic compounds **2a** and **d** presented a more intense dual fluorescence, when compared to their analogues. It is probably due to the oxygen in 1-position, which is more electronegative than sulphur and nitrogen. In



Scheme 4.

this way, the oxazole conformers E_{II}–E_{III} can be more stabilized, in spite of their analogues. For **2a–f** derivatives, it is presented in Scheme 4, the basic structure of the conformers which can be presented in solutions of (a) apolar and/or aprotic and (b) polar and/protic solvents. It is worth to mention in this scheme, that the ground and excited states are degenerated, since these energies depend on the solvent polarity and the non-ESIPT conformers (E_{II}–E_{IV}) present the same localization on the absorption and emission maximum.

The absorption spectra of **2g** and **h** are presented in Fig. 4 and show the absorption maximum at 337 and 351 nm, respectively. A very small shift on the absorption maximum could be detected (∼2 nm) to these dyes. The values of the molar extinction coefficients (10^4 l mol^{-1} cm^{-1}) are in agreement with π–π* transitions and the blue shift with increasing solvent polarity was also observed (Table 3). The results observed to the dyes **2g** and **h** cannot be taken as conclusive to discard the conformational equilibrium in solution in the ground state, since the conformers could absorb UV light at very close wavelength [42]. A solvent dependent dual fluorescence emission can be seen with the ESIPT band located around 475 and 500 nm and another blue shifted located at 390 nm to **2g** and **h**, respectively. These results are showing that the fluorescence emission is a powerful tool to discuss the conformational equilibrium in ground state even to dyes with a very close absorption maximum dependence on the solvent polarity. The conformational equilibrium in the ground state is probably between E_I–E_{III} conformers. Only the ESIPT band located at 468 nm can be seen in chloroform and dioxane to the dye **2h**.

Table 3 shows the quantum yield of the dyes **2g** and **h**, where dye **2g** (≈0.07) presents the higher one. It is probably due to an stabilization of the enol-*cis* conformer, caused by the acryloylamide group.

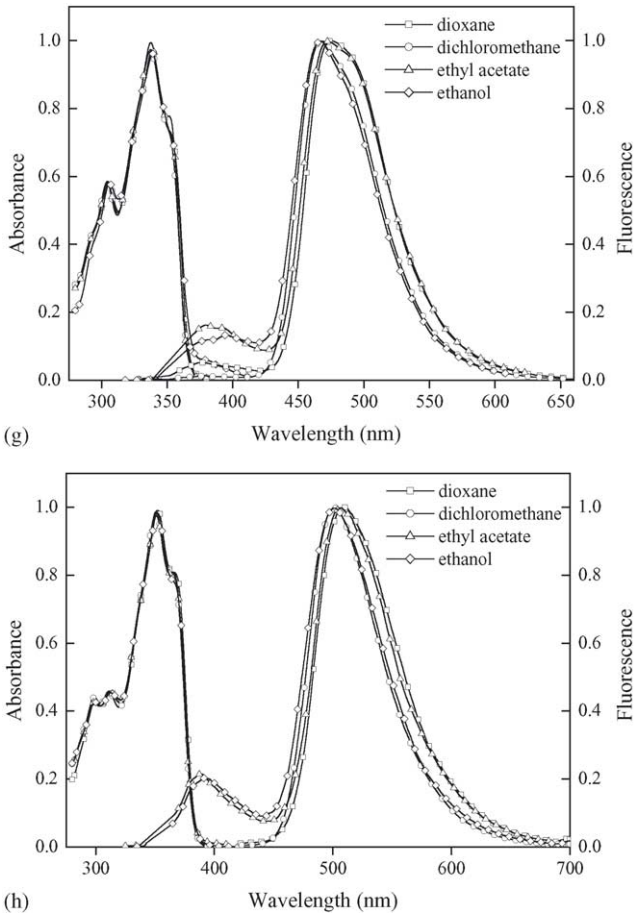


Fig. 4. Normalized absorption and fluorescence emission spectra of **2g** and **h**.

3.2. Polymer characterization

The polymerization of the benzazolylvinylene dyes with MMA lead new fluorescent ESIPT polymers with the dyes covalently bonded into the polymer chain. The PMMA and copolymers present similar values on the glass transition temperature (T_g). The results from thermogravimetric analysis are showing that the copolymers presents three well-defined decomposition processes, the first at around 110 °C which lies with some dye decomposition and the other ones at 270

Table 3
UV–vis and fluorescence emission data of the dyes **2g** and **h**

Dye	Solvent	λ_{max}^{abs} (nm)	$\varepsilon_{max} \times 10^{-4}$ (l mol^{-1} cm^{-1})	λ_{max}^{em} (nm)	$\Delta\lambda_{ST}^{keto}$ (cm^{-1})	$(\phi_{fl})_{enol}$	$(\phi_{fl})_{keto}$
2g	Acetonitrile	336	0.7	469	8440	0.0065	0.0056
	Benzene	339	3.6	474	8401	0.0122	0.1005
	Dioxane	338	7.9	474	8489	0.0101	0.0974
	Dichloromethane	337	1.8	468	8306	0.0039	0.1217
	Ethyl acetate	337	1.8	474	8576	0.0045	0.0415
	Ethanol	337	1.6	467	8260	0.0192	0.0683
	Methanol	337	3.6	464	8122	0.0108	0.0262
2h	Acetonitrile	350	4.0	497	8451	0.0043	0.0032
	Benzene	353	6.6	506	8566	0.0054	0.0455
	Dioxane	352	8.0	511	8840	0.0082	0.0271
	Dichloromethane	351	4.3	502	8570	0.0039	0.0423
	Ethyl acetate	351	2.8	506	8727	0.0013	0.0063
	Ethanol	351	3.9	501	8530	0.0105	0.0125
	Methanol	351	3.9	500	8490	0.0176	0.0087

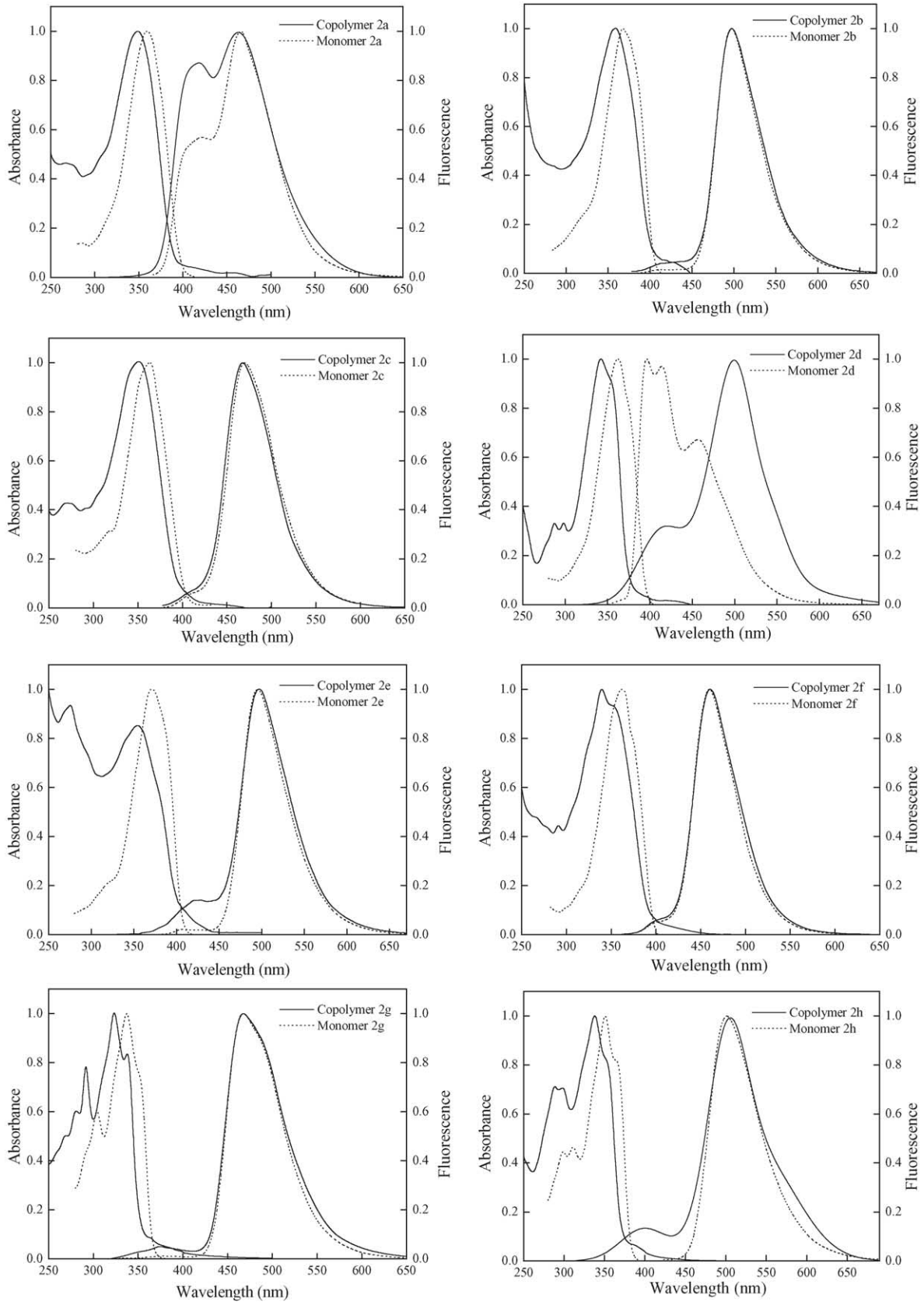


Fig. 5. Normalized absorption and fluorescence emission spectra of copolymers and monomers **2g** and **h**.

Table 4
Relevant data of the fluorescent copolymers **4a–f** and PMMA obtained by GPC ($\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$), DSC (T_g), TGA (T_d) UV–vis absorption (λ_{max}^{abs}) and fluorescence emission (λ_{max}^{em})

Sample	$\bar{M}_n \times 10^3$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$	T_d (°C)	T_g (°C)	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	$\Delta\lambda_{ST}^{keto}$ (cm^{-1})
PMMA	84	1.60	110; 282; 382	104	–	–	–
Copolymer **2a**	241	1.60	112; 264; 392	110	349	462	7008
Copolymer **2b**	245	1.61	116; 261; 395	108	359	498	7775
Copolymer **2c**	171	1.83	116; 263; 386	105	350	468	7204
Copolymer **2d**	280	1.60	106; 267; 388	103	342	497	9119
Copolymer **2e**	188	1.62	108; 261; 388	111	355	497	8048
Copolymer **2f**	139	1.61	127; 279; 388	98	339	460	7759
Copolymer **2g**	156	1.51	113; 247; 392	105	323	468	9592
Copolymer **2h**	93	1.45	268; 382	106	338	504	9744

and 380 °C, similar to the PMMA, related to the polymer chain decomposition. (Table 4).

The normalized absorption spectra and fluorescence emission of the copolymers **2a–h** in dichloromethane are presented in Fig. 5. The monomers are also depicted for comparison. In all copolymers, a blue shift could be observed on the absorption spectra (9–23 nm) indicating that the monomer are covalently attached into the polymer matrix, as expected. The values of the molar extinction coefficients are also in agreement with π–π^* transitions (10^4 l mol^{-1} cm^{-1}). The fluorescence emission spectra of the copolymers **2a–c** and **2e–h** show no changes in its long-wavelength maximum when compared with the corresponding monomers. However, the copolymer **2d** which show the dual fluorescence emission as already observed to the correspondent monomer, presents the band ascribed to the ESIPT mechanism (~500 nm) red-shifted if compared to the monomer ESIPT band (~470 nm), probably due to the interaction of the phenolic OH with the polymer matrix.

4. Conclusions

Eight new fluorescent monomers were synthesized, purified until optical purity grade and characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, infrared, UV–vis and fluorescence spectroscopy. The benzoxazole and benzimidazole monomers are fluorescent in the blue-purple region and the benzothiazole monomers in the green region. The monomers presented a Stokes shift between 51 and 159 nm. The absorption maximum dependence on the solvent polarity and the dual fluorescence indicated a conformational equilibrium in solution in the ground state. The emission at long wavelength (ESIPT band) is due to an excited keto tautomer, which arises from an enol-*cis* (E_I) conformer in the excited state. The blue shifted bands are due to conformational forms with a normal relaxation. The new monomers showed to be very sensitive to solvent polarity. All the synthesized monomers were totally soluble in MMA and were used to produce eight new polymers. The resultant copolymers are transparent in the visible and present fluorescence when illuminated with UV radiation. The new monomers and polymers showed to be very attractive to be used as new fluorescent materials.

Acknowledgements

We are grateful for financial support and scholarships from the Brazilian agencies CNPq, FAPERGS and CAPES. Special thanks to Dr. Leandra Franciscato Campo for support in the polymerization reactions.

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