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Cationic 3*H*-indolium dyes by ring-opening of benzo[1,3]oxazine

Yaroslav Prostota, Paulo J. Coelho*

Centro de Química – Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal

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ABSTRACT

The reaction of 2-methylbenzo[1,3]oxazine with (hetero)aromatic aldehydes under acid catalysis afforded directly polymethine dyes, formed by a thermal ring-opening of the oxazine cycle followed by condensation with the aldehydes. These dyes have the structure of a cationic thermally stable coloured open form of a photochromic benzo[1,3]oxazine and do not undergo ring-closure to afford the closed form again, even under basic treatment. All of the dyes showed reversible acidochromic properties.

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1. Introduction

Benzo[1,3]oxazines are a family of molecular switches that combine two fused heterocyclic rings, indoline and oxazine, in their molecular skeleton [1]. These molecules exhibit thermally reversible photochromic properties with a very fast switching speed between the uncoloured (closed) and coloured (open) states [2].

UV light irradiation leads to the cleavage of the C–O bond at the junction of the two heterocycles and consequent opening of the [1,3]oxazine ring with formation, in less than 20 ns, of a zwitterionic species incorporating a 3*H*-indolium cation and a 4-nitrophenolate anion. This photochemical process is accompanied by the appearance of an absorption band around 430–440 nm typical of the 4-nitrophenolate chromophore (Scheme 1). The coloured species usually have a very short lifetime (<60 ns) and revert spontaneously to the uncoloured closed benzo[1,3]oxazine with first order kinetics. Therefore, a complete cycle can be performed normally in less than 100 ns [3,4].

When a 2-phenylethenyl fragment is attached to the chiral C-2 atom, the photochemical ring-opening of the oxazine ring allows the conjugation between the π-systems of the 3*H*-indolium and the 2-phenylethenyl fragment leading to a polymethine-type chromophore which results in a shift of the absorption maxima of the entire molecule to longer wavelength [5]. Therefore the ring-opening of these 2-substituted benzo[1,3]oxazines generates two different absorption bands due to the formation of two chromophoric systems in the same zwitterionic molecule: one located at 440 nm assigned to the 4-nitrophenolate anion and the other around 550 nm due to the 2-substituted-3*H*-indolium cation with extended conjugation (**A** in Scheme 2). The position of the longer wavelength band can be tuned by the introduction of some substituents in the aromatic ring without considerably affecting the photochromic performance of the benzo[1,3]oxazine. Nevertheless, changes in the phenolate chromophore or in the 3*H*-indolium fragment may completely prevent the photoinduced ring-opening [6,7].

^{1}H NMR studies on some benzo[1,3]oxazines revealed that the two diastereotopic methyl groups of the indoline ring, adjacent to the chiral C-2 centre, resonate as a single and broad peak at 1.3–1.6 ppm. This indicates that the two enantiomers of the ring-closed form exchange rapidly on the ^{1}H NMR time-scale and a thermal equilibrium between the closed and opened forms must exits at room temperature [3]. This equilibrium can be reversibly shifted towards the opened form by the addition of either acid of base. Under acidic conditions (e.g. addition of CF_3COOH) the phenolate anion is protonated displacing the equilibrium position towards the formation of the stable opened form **B** (Scheme 2), that will show only the longer wavelength absorption band assigned to the 3*H*-indolium polymethine-like chromophoric system. The addition of base (few equivalents of Bu_4NOH) has an opposite effect: the hydroxyl ion adds to the 3*H*-indolium cation with formation of a stable hemiaminal which breaks the conjugation of this

* Corresponding author. Tel.: +351 259 350284; fax: +351 259 350480.
E-mail address: pcoelho@utad.pt (P.J. Coelho).

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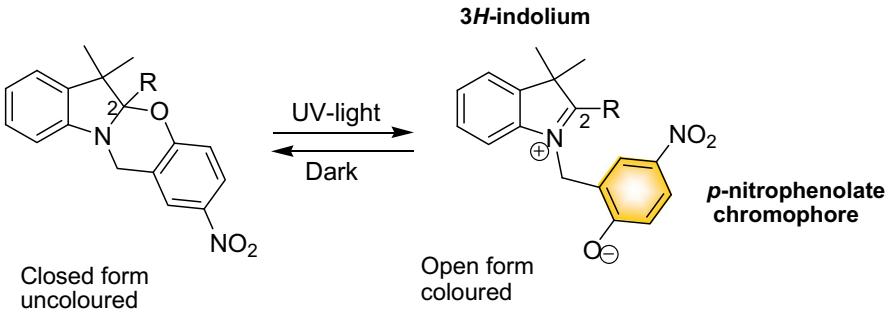
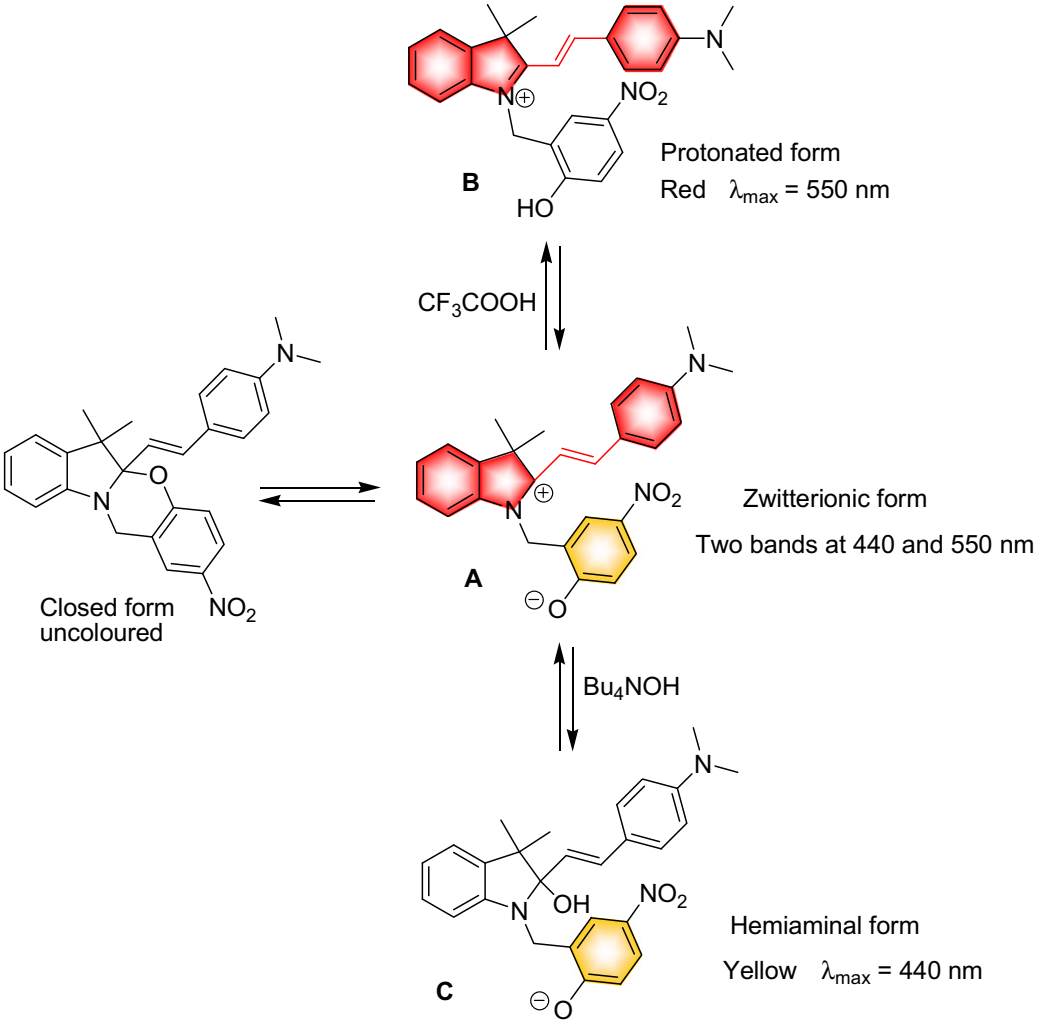


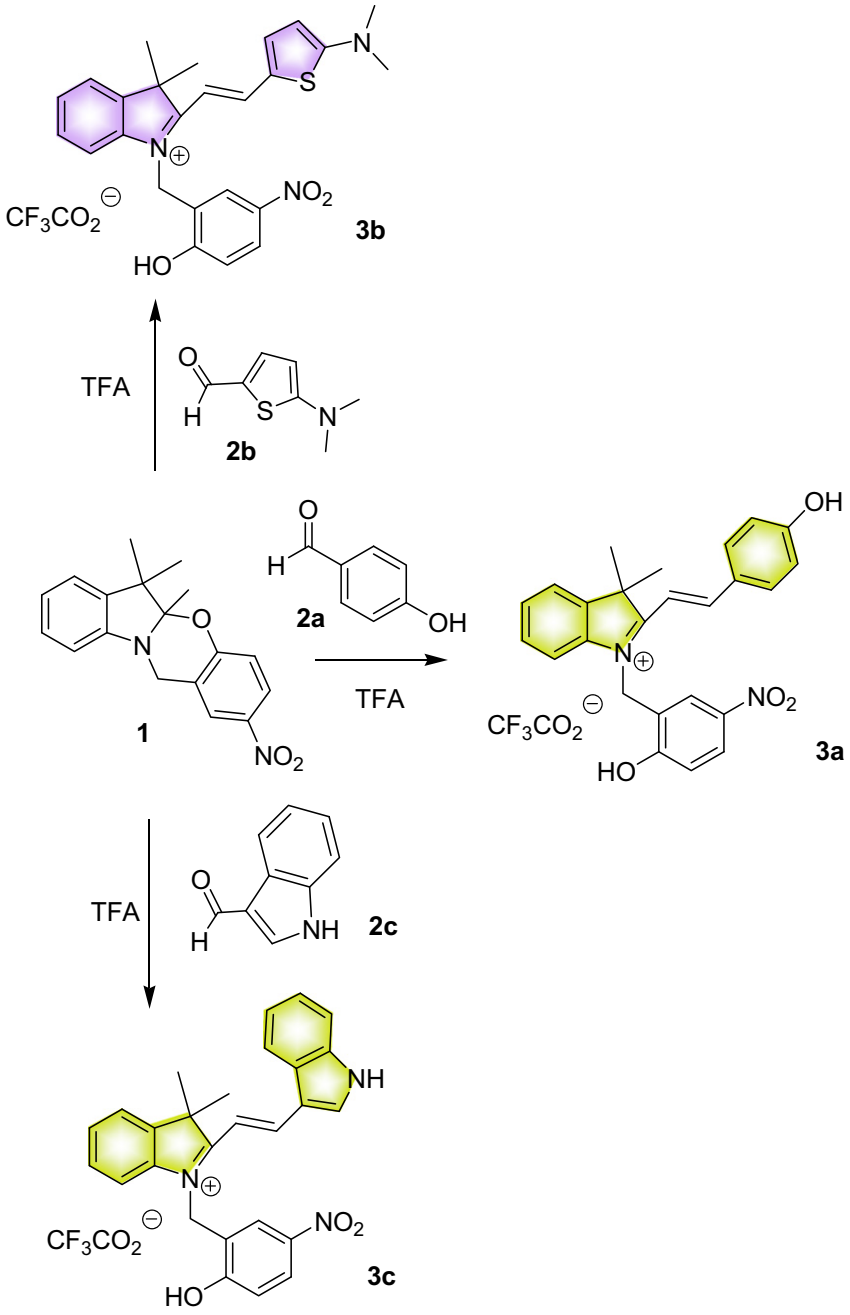
Scheme 1. Photochromic equilibrium for benzo[1,3]oxazines.

part of the molecule. As a result, in basic medium, only the 440 nm absorption band characteristic of the 4-nitrophenolate anion is observed (**C** in Scheme 2). Both processes are reversible and the benzo[1,3]oxazines can be switched between these states with no signs of degradation [3].

The extension of the conjugation through the linkage of a substituent (R) at the 2-position of the benzo[1,3]oxazine has also an effect on the thermal stability of the opened bichromophoric dye leading to an increase of their lifetime when strong electron-donating groups become part of the conjugated system: for instance, a 4-dimethylaminophenyl group present at the chiral C-2 atom leads to a 1000 times increase on the lifetime of the photogenerated coloured species and, accordingly, these 2-substituted benzo[1,3]oxazines operate in the microsecond time scale [7]. However, when some conjugated systems are linked to the chiral oxazine centre, the spontaneous opening of the oxazine ring occurs with formation of stable dyes with a ring-opened oxazine zwitterionic structure [8,9]. These dyes exhibit two absorption bands in the visible spectrum and do not undergo ring-closure even in basic medium. Such type of stabilization of the coloured open form was



Scheme 2. Ring-opening of 2-(4′-dimethylaminostyryl)benzo[1,3]oxazine in basic and acid medium.



Scheme 3. Synthesis of dyes **3a**–**c**.

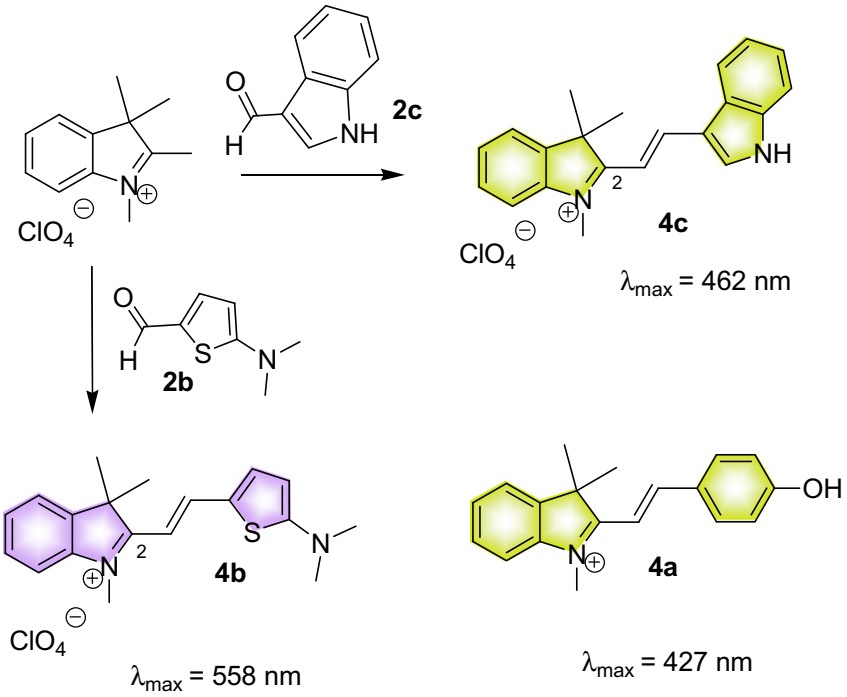
achieved when pyrrole, indoline or julolidine systems were linked to the benzo[1,3]oxazine and suggests that it is possible to control the lifetime of the usually short lived open species through electronic effects [8–10]. The increase in the solvent polarity can also increase the lifetime of the ring-opened isomers [11] or even lead to the formation of equilibrium mixtures of the closed and open forms at room temperature [9].

In order to study the influence of other electron-rich systems on the equilibrium between the ring-closed and ring-opened forms we introduced 4-hydroxyphenyl, 5-dimethylaminothiophenyl and 3-indolyl substituents on the C-2 position of the benzo[1,3]oxazine and studied the spectroscopic and acidochromic properties of these new compounds.

2. Results and discussion

2.1. Synthesis

The benzo[1,3]oxazine core with the fused indoline and oxazine rings can be easily prepared by N-alkylation of 2-substituted-3*H*-indoles with 2-chloromethyl-4-nitrophenol in acetonitrile followed by spontaneous intramolecular oxazine cyclization. This reaction is quite reliable and has been used for the synthesis of many compounds having different substituents [3–6]. Alternatively, the methyl group at C-2 of the benzo[1,3]oxazine **1** can be condensed with aromatic aldehydes to produce ring-closed oxazines able to produce short-lived dyes with extended conjugation after UV



Scheme 4. Synthesis of model 3*H*-indolium dyes **4b**–**c**.

activation [7,9,10]. In special cases, depending on the nature of the aromatic aldehydes, this reaction afforded directly stable dyes with an oxazine ring-opened structure [8–10].

The condensation of 2-methylbenzo[1,3]oxazine **1** with the aromatic aldehydes **2a**–**c** was performed in CH_3CN in the presence of trifluoroacetic acid (TFA) and afforded, after 3–12 days at reflux, the dyes **3a**–**c** with a ring-opened oxazine structure (Scheme 3). The NMR spectra of the opened and closed forms of benzo[1,3] oxazines are very similar, nonetheless there are some specific resonances typical of each form [3,4]. The ^{1}H NMR spectra of the new dyes **3a**–**c** reveals resonances that can be assigned exclusively to the ring-opened form: in particular the two methyl groups of the indoline ring resonate at the same chemical shift, 1.73–1.46 ppm (s, 6H) which suggests that the adjacent C-2 is no longer a chiral centre; the CH_2N signal was found between 5.81 and 4.94 ppm shifted from his usual value in the benzo[1,3]oxazines (around 4.50 ppm) [3,4]; two low field phenolic signals were found for compound **3a** at 12.15 and 11.1 ppm; a low field signal was found in the ^{13}C NMR spectra, between 174 and 183 ppm, which can be assigned to C-2 of the 3*H*-indolium moiety [8]. ^{19}F NMR spectroscopy established the presence of trifluoroacetate as the counterion which indicates that the dyes **3a**–**c** exists in the cationic form. These data, along with the results from mass spectrometry, unambiguously confirmed that these dyes possess a ring-opened 3*H*-indolium cationic structure and are thus probably formed by thermal ring-opening of the oxazine cycle of compound **1** and subsequent reaction of the active 2-methyl group of the 3*H*-indolium cation with the aldehydes, leading to the polymethine dyes **3a**–**c**.

To compare the similarity of the chromophore skeleton, the model 3*H*-indolium dyes **4b**–**c** were prepared by condensation of 1,2,3,3-tetramethyl-3*H*-indolium perchlorate with aldehydes **2b**–**c** (Scheme 4). These compounds exhibit some NMR similarities with the dyes **3b**–**c**, in particular, the low field signals at 180–173 ppm in their ^{13}C NMR spectra, which is characteristic of the 3*H*-indolium C-2 carbon atom. The synthesis and some spectroscopic properties of the model compound **4a** have already been described in the literature [10,12].

2.2. Acidochromic properties of dyes *3a–c*

The steady state absorption spectrum of dye **3a** (1.0×10^{-5} M) (Fig. 1) shows an intense absorption band in the visible range, at 438 nm, which resembles the ground state absorption of model compound **4a** (λ_{max} = 427 nm). Addition of one drop of base (Bu_4NOH, 1 M in MeOH) to a CH_3CN solution of dye **3a** leads to the formation of an intense red colour that turns in few seconds to yellow with the absorption maxima at 434 nm.

Further addition of base does not change the position of absorption maxima. These results suggests that upon addition of base the phenolic proton of the 3*H*-indolium cation is removed leading to an intermediate merocyanine structure (**A**) which is known to absorb at longer wavelengths (λ_{max} = 540 nm) (Scheme 5) [12]. This species is unstable and through proton exchange is probably converted to the zwitterionic form (**B**) which has two chromophoric systems, both absorbing in the same range of wavelength, around 434 nm (Scheme 5). Subsequent addition of an aqueous solution of

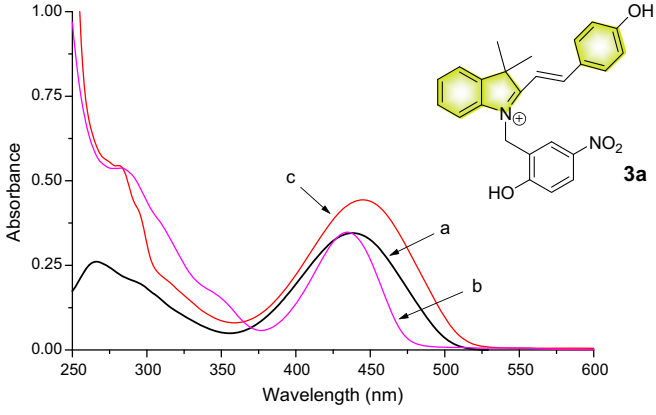
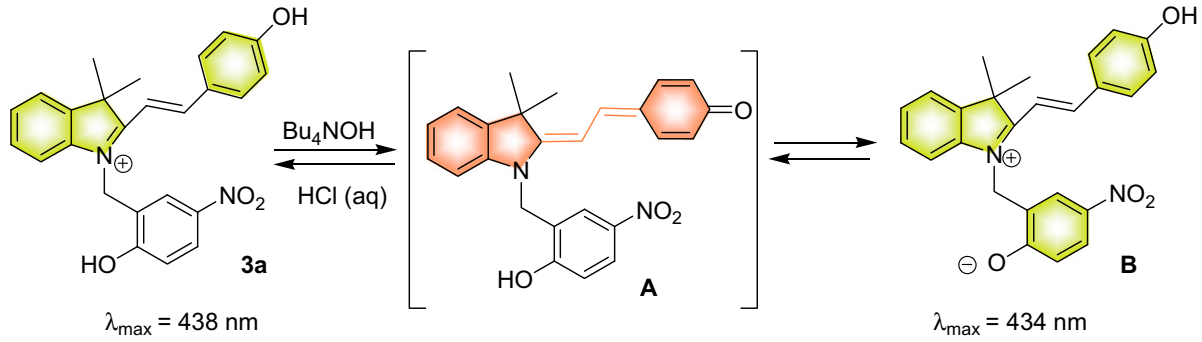


Fig. 1. Absorption spectra of the compound **3a** in acetonitrile (1.0×10^{-5} M) (**a**); after addition of 10 eq. of $Bu_4N^+OH^-$ (**b**); and subsequent addition of aqueous HCl (5%) (**c**).



Scheme 5. Acid-base equilibrium for dye **3a**.

HCl(aq) lead to a small bathochromic shift of the λ_{max} (+7 nm) probably due to the regeneration of compound **3a**, to the change of the counterion and also due to some solvatochromism.

Dye **3b** shows a strong and sharp absorption band at 560 nm which resembles the absorption of the model compound **4b** (λ_{max} = 558 nm) and is due to the extended conjugation in the 3*H*-indolium fragment (Fig. 2). Addition of base leads to the extinction of this violet band and the appearance of a broad one at 432 nm.

The disappearance of the band at 550 nm is due to the addition of hydroxide ion to the 3*H*-indolium cation to give a hemiaminal structure, thus breaking the conjugation between the indoline and the thiophene systems, while the new band at 420 nm can be assigned to the formation of the 4-nitrophenolate anion. This process is reversible and upon subsequent addition of acid the hemiaminal is rapidly converted to the dye **3b** (Scheme 6).

In CH_3CN solution dye **3c** exhibits a broad absorption band at 486 nm that is similar to the absorption of the model 3*H*-indolium dye **4c** (λ_{max} = 462 nm) (Fig. 3). Addition of base leads to the appearance of two bands at 434 and 494 nm that suggests the formation of a zwitterionic open form of the benzo[1,3]oxazine system with two chromophores, the 4-nitrophenolate (λ_{max} = 434 nm) and the 3*H*-indolium cation (λ_{max} = 494 nm), instead of the possible hemiaminal structure (Scheme 7).

This bichromophoric dye is remarkably stable and does not undergo ring-closure to form a benzo[1,3]oxazine structure. Further addition of acid led to the appearance of a broad band at 488 nm which may correspond to the renewal of the cationic structure for the dye **3c**. The process is reversible and the dye can be switched between these two states upon addition of base or acid.

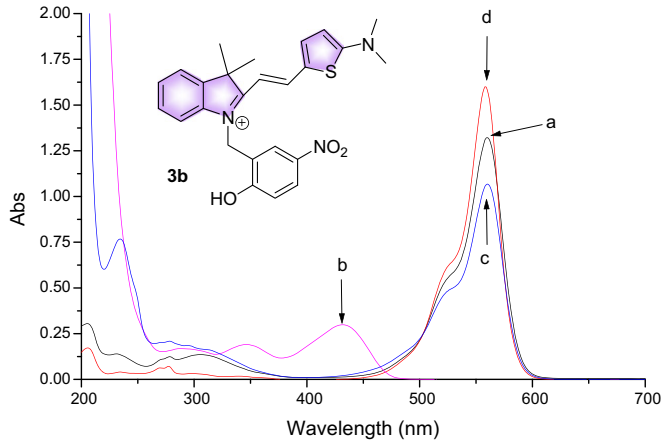


Fig. 2. Absorption spectra of the compound **3b** (**a**); after addition of 10 eq. of $Bu_4N^+OH^-$ (**b**); subsequent addition of aqueous HCl (5%) (**c**); and the model dye **4b** (**d**) in acetonitrile (1.0×10^{-5} M).

3. Conclusion

The reaction of 2-methylbenzo[1,3]oxazine with some (hetero) aromatic aldehydes affords polymethine dyes with a conjugated chain corresponding to cationic open form of the benzo[1,3]oxazine system, which do not undergo intramolecular ring-closure in basic medium. These dyes show reversible acidochromic behaviour allowing switching between the 3*H*-indolium cation with extended conjugation and the 4-nitrophenolate anion chromophores. Dye **3c** formed, after basic treatment, a stable zwitterionic bichromophoric opened form with two absorption bands assigned to the polymethine 3*H*-indolium cation and the 4-nitrophenolate anion chromophores.

4. Experimental

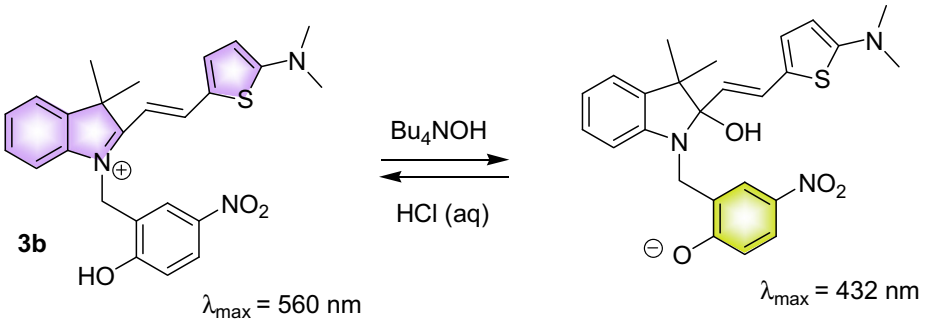
4.1. General

2-Nitro-5a-phenyl-6,6-dimethyl-5a,6-dihydro-12*H*-indolo[2,1-*b*][1,3]benzooxazine **1** and 5-dimethylamino-thiophene-2-carbaldehyde **2b** were prepared according to literature procedures [1,13]. Solvents were of analytical grade and the acetic anhydride was previously distilled. A 1 M solution $Bu_4N^+OH^-$ in methanol was used. All reactions were monitored by thin-layer chromatography on aluminium plates coated with Merck silica gel 60 F_{254} (0.25 mm). ^1H and ^{13}C NMR spectra were recorded at 298 K on a Bruker ARX400 spectrometer (at 400.13 and 100.62 MHz). The new compounds were determined to be >95% pure by ^1H NMR spectroscopy. IR spectra were obtained on a Unicam Research Series FTIR spectrometer using KBr pellets. Wavenumbers (λ_{max}) are reported in cm^{-1}. UV–Vis spectra were recorded on a Perkin–Elmer Lambda 25 spectrophotometer in spectral grade acetonitrile. High resolution electrospray ionization time-of-flight (ESI-TOF) mass spectra and electron impact time-of-flight (EI-TOF) mass spectra were measured with a VG AutoSpec M spectrometer. Melting points were determined in open capillary tubes in a Buchi 535 melting point apparatus and are uncorrected.

4.2. Synthesis of dyes *3a–c*

4.2.1. *1-(2′-Hydroxy-5′-nitro-benzyl)-3,3-dimethyl-2-[4′-hydroxystyryl]-3H-indolium trifluoroacetate* ***3a***

A solution of **1** (0.20 g, 0.65 mmol), **2a** (0.090 g, 0.74 mmol) and CF_3CO_2H (0.023 mL, 0.30 mmol) in CH_3CN (20 mL) was heated under reflux for 3 days. After cooling to ambient temperature, the reaction mixture was evaporated to dryness under reduced pressure and the resultant residue dissolved in hot CH_2Cl_2 (15 mL). The crystalline residue formed at cooling was filtered off and washed consequently with CH_2Cl_2 (3 mL) and Et_2O (10 mL) to afford **3a** (0.22 g, 64%) as an orange solid. Mp. 219–222 °C. IR: 522, 715, 832,



Scheme 6. Acid-base equilibrium for dye **3b**.

1162, 1230, 1517, 1568, 1664, 2987, 3083, 3393. ^{1}H NMR (DMSO-d_6): 1.79 (s, 6H), 5.90 (broad s, 2H), 6.94 (d, J = 8.4, 2H), 7.02 (d, J = 9.0, 1H), 7.51 (broad s, 2H), 7.71 (broad s, 2H), 7.83 (broad s, 1H), 8.07 (broad s, 2H), 8.11 (dd, J = 9.0, 2.6, 1H), 8.37 (m, 1H), 8.38–8.50 (broad s, 1H), 11.06 (broad s, 1H), 12.15 (broad s, 1H). ^{13}C NMR (DMSO-d_6): 26.0, 45.5, 51.8, 54.8, 109.8, 114.81, 116.1, 116.6, 118.4, 120.7, 122.9, 125.4, 125.9, 126.1, 128.8, 133.8, 139.4, 141.1, 142.9, 162.4, 164.0, 156.0, 183.0 ^{19}F NMR (DMSO-d_6): −73.66 (CF_3); HRMS (TOF ESI): calcd for $[C_{25}H_{23}N_2O_4]^+$: 415.1652; found: 415.1634.

*4.2.2. 1-(2′-Hydroxy-5′-nitro-benzyl)-3,3-dimethyl-2-[(5-dimethylaminothiophen-2-yl)vinyl]-3H-indolium trifluoroacetate **3b***

A solution of **1** (0.17 g, 0.55 mmol), **2b** (0.090 g, 0.58 mmol) and CF_3CO_2H (0.023 mL, 0.30 mmol) in CH_3CN (20 mL) was heated under reflux for 12 days. After cooling to ambient temperature the crystalline residue formed was filtered off and washed consequently with EtOAc (3 mL), hexanes (3 mL) and Et_2O (10 mL) to afford **3b** (0.16 g, 52%) as a green solid with a metallic lustre. Mp. 222–224 °C. IR: 592, 706, 749, 810, 840, 906, 1019, 1075, 1132, 1189, 1263, 1315, 1380, 1463, 1541, 1589, 1667, 3095, 3385. ^{1}H NMR (DMSO-d_6): 1.68 (s, 6H), 3.34 (s, 6H), 5.39 (s, 2H), 6.10 (d, J = 14.0, 1H), 6.77 (d, J = 5.0, 1H), 7.04 (d, J = 9.0, 1H), 7.25 (t, J = 7, 1H), 7.37–7.45 (m, 2H), 7.62 (d, J = 7.0, 1H), 7.98 (d, J = 5.0, 1H), 8.03 (m, 1H), 8.09 (d, J = 9.0, 1H), 8.31 (d, J = 14.0, 1H). ^{13}C NMR (DMSO-d_6): 27.1, 42.1, 43.2, 48.6, 97.9, 111.1, 113.3, 115.7, 118.0, 122.2, 124.3, 124.5, 125.6, 127.1, 128.3, 139.3, 140.3, 142.2, 142.4, 148.8, 162.0, 172.7, 174.2. ^{19}F NMR ($CDCl_3$): −73.39 (CF_3); HRMS (TOF ESI): calcd for $[C_{25}H_{26}N_3O_3S]^+$: 448.1689; found: 448.1684.

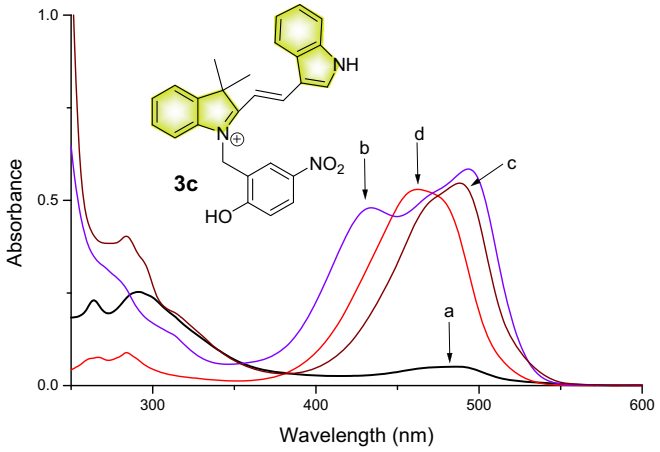


Fig. 3. Absorption spectra of the compound **3c** (**a**); after addition of 10 eq. of $Bu_4N^+OH^-$ (**b**); subsequent addition of aqueous HCl (5%) (**c**); and the model dye **4c** (**d**) in acetonitrile (1.0×10^{-5} M).

*4.2.3. 1-(2′-Hydroxy-5′-nitro-benzyl)-3,3-dimethyl-2-[(1H-indol-3-yl)vinyl]-3H-indolium trifluoroacetate **3c***

A solution of **1** (0.20 g, 0.65 mmol), **2c** (0.10 g, 0.69 mmol) and CF_3CO_2H (0.023 mL, 0.30 mmol) in CH_3CN (20 mL) was heated under reflux for 9 days. After cooling to ambient temperature the reaction mixture was evaporated to dryness under reduced pressure. The resultant residue was dissolved in CH_2Cl_2 (25 mL), washed with KOH (40 mL, 0.05 M), water (40 mL), dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was crystallized from a mixture of EtOH:acetone:CH_3CN (5:2:1 v/v), filtered off and washed with Et_2O (3 mL) to afford **3c** (0.10 g, 28%) as a red solid. Mp. 205–207 °C. IR: 584, 697, 749, 815, 1027, 1089, 1141, 1189, 1219, 1293, 1415, 1463, 1571, 3083, 3373. ^{1}H NMR (DMSO-d_6): 1.46 (s, 6H), 4.94 (s, 2H), 6.52 (d, J = 16.0, 1H), 6.79 (d, J = 9.0, 1H), 6.96 (t, J = 7.0, 1H), 7.06–7.22 (m, 4H), 7.33 (d, J = 7.0, 1H), 7.43 (d, J = 8.0, 1H), 7.32–7.45 (br.s, 1H, merged with two other signals), 7.85–7.87 (m, 2H), 7.91 (dd, J = 9.0, 3.0, 1H), 8.05 (d, J = 3.0, 1H). ^{13}C NMR (DMSO-d_6): 18.5, 23.8, 26.4, 30.6, 49.5, 110.4, 12.8, 144.0, 117.7, 120.1, 121.0, 121.2, 122.3, 122.7, 124.0, 124.7, 124.9, 127.8, 136.8, 138.4, 139.2, 145.1. ^{19}F NMR ($CDCl_3$): −75.21 (CF_3); HRMS (TOF ESI): calcd for $[C_{27}H_{24}N_3O_3]^+$: 438.1812; found: 438.1807.

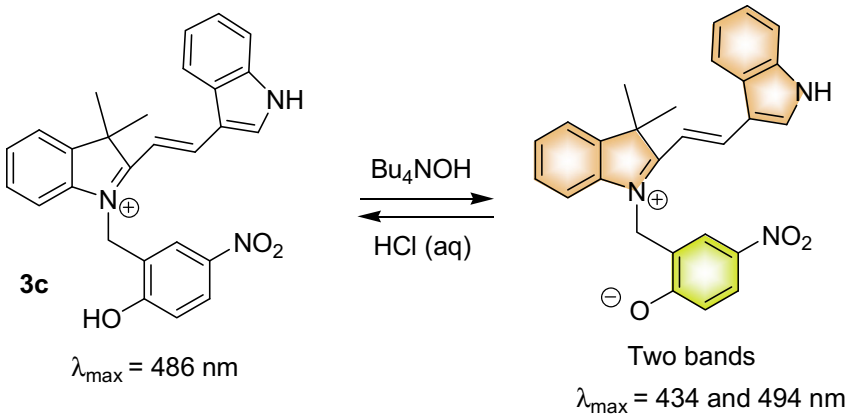
*4.3. Synthesis of model dyes **4b–c***

*4.3.1. 1,3,3-Trimethyl-2-[2-(5-dimethylaminothiophen-2-yl)vinyl]-3H-indolium perchlorate **4b***

A solution of **2b** (0.11 g, 0.73 mmol) and 1,2,3,3-tetramethyl-3*H*-indolium perchlorate (0.20 g, 0.73 mmol) in freshly distilled acetic anhydride (5 mL) was heated under reflux for 3 min. The crystalline residue formed upon cooling was filtered off, washed with EtOAc (5 mL) and Et_2O (5 mL) to afford **4b** (0.20 g, 67%) as blue crystals with a metallic lustre. Mp. 229–231 °C (dec.). IR: 584, 619, 702, 797, 911, 1081, 1207, 1259, 1311, 1384, 1411, 1476, 1551, 2925, 3373. ^{1}H NMR (DMSO-d_6): 1.66 (s, 6H), 3.31 (s, 6H), 3.61 (s, 3H), 6.04 (d, J = 13.8, 1H), 6.69 (m, 1H), 7.23 (m, 1H), 7.38 (m, 2H), 7.58 (d, J = 7.0, 1H), 8.00 (m, 1H), 8.33 (d, J = 13.8, 1H). ^{13}C NMR ($CDCl_3$): 26.8, 31.1, 42.9, 48.9, 97.5, 111.0, 111.8, 122.2, 124.8, 126.1, 128.2, 140.8, 142.5, 142.7, 148.2, 173.1, 173.9. HRMS (TOF ESI): calcd for $[C_{29}H_{23}N_2S]^+$: 311.1577; found: 311.1583.

*4.3.2. 1,3,3-Trimethyl-2-[2-(1H-indol-3-yl)vinyl]-3H-indolium perchlorate **4c***

A solution of **3c** (0.11 g, 0.73 mmol) and 1,2,3,3-tetramethyl-3*H*-indolium perchlorate (0.20 g, 0.73 mmol) in freshly distilled acetic anhydride (10 mL) was heated under reflux for 3 min. The crystalline residue formed upon cooling was filtered off, washed with Et_2O (5 mL) and recrystallized from CH_3CN:MeOH 2:1 v/v mixture to afford **4c** (0.18 g, 61%) as a orange solid. Mp. > 300 °C (dec.). IR: 562, 619, 758, 819, 928, 950, 1102, 1236, 1301, 1328, 1406, 1432, 1475, 1593, 3060, 3260. ^{1}H NMR (DMSO-d_6): 1.80 (s, 6H), 4.00 (s,



Scheme 7. Acid-base equilibrium for dye **3c**.

3H), 7.19 (d, $J = 16.0$, 1H), 7.37–7.41 (m, 2H), 7.49 (t, $J = 7.4$, 1H), 7.57 (t, $J = 7.8$, 1H), 7.61–7.63 (m, 1H), 7.75 (d, $J = 7.9$, 1H), 7.79 (d, $J = 7.2$, 1H), 8.27 (dd, $J = 6.0$, 3.0, 1H), 8.66 (s, 1H), 8.69 (d, $J = 16.0$, 1H). ^{13}C NMR (DMSO-d_6): 26.2, 32.8, 50.7, 105.0, 113.4, 113.5, 115.8, 121.3, 122.5, 123.1, 124.3, 124.5, 127.4, 128.6, 138.3, 140.5, 142.0, 142.3, 148.8, 180.1. HRMS (TOF-ESI): calcd for $[C_{21}H_{21}N_2]^+$: 301.1699; found: 301.1696.

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