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Bichromophoric dye derived from benzo[1,3]oxazine system

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ABSTRACT

The reaction of 2-methylbenzo[1,3]oxazine with julolidine-9-carbaldehyde under acid catalysis afforded an highly coloured blue dye with an intense absorption at 591 nm. NMR and UV–Vis analysis showed that this compound has an opened oxazine structure with a polymethine-type chromophore, corresponding to a protonated thermally stable coloured form of photochromic benzo[1,3]oxazines that are known to be unstable at room temperature with lifetimes in the ns timescale. In basic medium this dye is converted into a stable opened zwitterionic form of photochromic benzo[1,3]oxazines with two absorption maxima at 410 and 587 nm assigned to conjugated 3*H*-indolium and 4-nitrophenolate chromophores respectively.

1. Introduction

Benzo[1,3]oxazines are an important class of molecules switches with exceptional fatigue resistance and fast switching speeds. Although their first synthesis was reported more than two decades ago [1], their photochromic properties were discovered only in 2005 [2]. UV light irradiation of these uncoloured molecules leads in less than 6 ns to the heterolytic cleavage of the C–O bond and consequent opening of the [1,3]oxazine ring with formation of a coloured zwitterionic species incorporating a 3*H*-indolium cation and a 4-nitrophenolate that absorbs strongly around 430–440 nm (Scheme 1). After the light pulse, the photogenerated coloured isomer reverts thermally to the uncoloured original state, usually within 15–60 ns with first-order kinetics. This particular photochromic system is remarkably stable and tolerates several thousand of switching cycles without significant degradation, even in the presence of molecular oxygen [2].

The nature of the R group has an important effect on the photochromic properties of these compounds. If R is an aromatic ring, the opening of the oxazine ring generates two chromophores: the yellow 4-nitrophenolate and the 2-aryl-3*H*-indolium cation that absorbs between 430 and 590 nm depending upon the substituents present in the aromatic ring. When R is a 4-dimethylaminophenyl group both chromophores absorb in the visible region near 440 nm and a single band is observed, however when a 4-dimethylaminostyryl group is attached at C-2, the ring-opened photoisomer shows two different absorption bands located at 440 nm and 550 nm assigned to the 4-nitrophenolate anion and the conjugated 4-dimethylaminostyryl-3*H*-indolium cation, respectively [3].

On the other hand, due to the zwitterionic character of the open form, these strong donating groups, at the 2-position of the 3*H*-indolium cation, have a significant effect on the stability of the coloured open form, increasing their lifetime up to 1000 times. For these benzo[1,3]oxazines with extended conjugation, the switching between the two forms can be performed in the μs timescale [3]. In contrast, substituents such as *p*-nitrophenyldiazenyl, on the *para* position of the phenolate chromophore, biphenyl on the oxazine chiral centre or methoxy, nitro and *trans*-stilbenylvinyl on the 3*H*-indole fragment, prevents the photoinduced ring opening of the oxazine ring [4,5].

As expected, the stability of the open form is also sensitive to the solvent polarity and increases with a transition from acetonitrile to ethanol or DMSO. In DMSO, a solvent with an high ability to complex organic cations, the lifetime of the zwitterionic open form of a naphtho [1,3]oxazine increased to 159 μs [6]. The increase in the solvent polarity can also lead to a shift in the equilibrium between the ring-closed and the ring-opened isomers: the conjugated linkage of a coumarin to the oxazine chiral C-2 atom led to a photochromic oxazine that exists predominantly in the closed form in acetonitrile, but the corresponding steady state absorption

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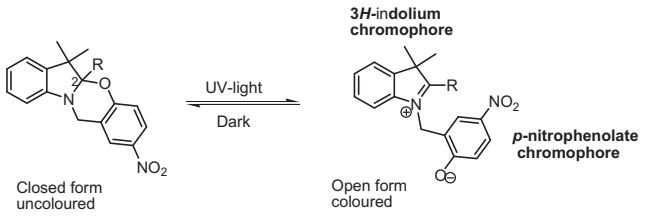
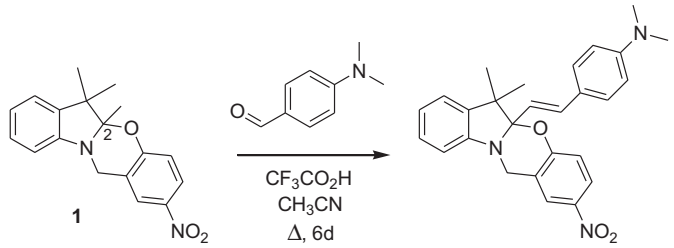


Scheme 1. Photochromic equilibrium for benzo[1,3]oxazines.



Scheme 3. Synthesis of 2-styrylbenzo[1,3]oxazines.

spectra spectrum in methanol shows the characteristic absorption of the 3*H*-indolium chromophore at 586 nm suggesting the presence of both ring-closed and ring-opened isomers at equilibrium in a 93:7 ratio [7].

The [1,3]oxazine cycle of these compounds can also be reversibly opened in acid or basic medium [8]. The addition of Bu_4NOH to benzo[1,3]oxazines leads to the opening of the oxazine ring followed by further reaction with the hydroxyl ion, with formation of a stable hemiaminal compound with the concomitant appearance of a strong absorption around 440 nm characteristic of the 4-nitrophenolate anion (Scheme 2).

In strong acidic conditions (e.g. addition of CF_3COOH) the [1,3] oxazine ring opens to generate a coloured conjugated fragment and a protonated 4-nitrophenol. This transformation allows the conjugation between the π-system of the 3*H*-indolium fragment and the aromatic substituent at C-2 leading to a polymethine-type chromophore resulting in a shift in the absorption to longer wavelengths in the visible region (λ_{max} = 550 nm), while the 4-nitrophenol has the main absorption in the UV region (Scheme 2).

The chemical and photochemical behaviour of these compounds suggests that it is possible to increase the stability of the zwitterionic open form, especially through the introduction of conjugated substituents with strong electron-donating character. A significant decrease in the ultrafast switching speed between the ring-closed and the ring-opened isomers could lead to the visual observation of the photochromic phenomena at room temperature and thus expand the practical applications of these compounds. With this idea in mind we explored the introduction, at carbon C-2, of a conjugated chain bearing the julolidine group which is known to have a strong electron-donating character probably related to the restricted rotation around the C(sp^2)–N bond [9,10].

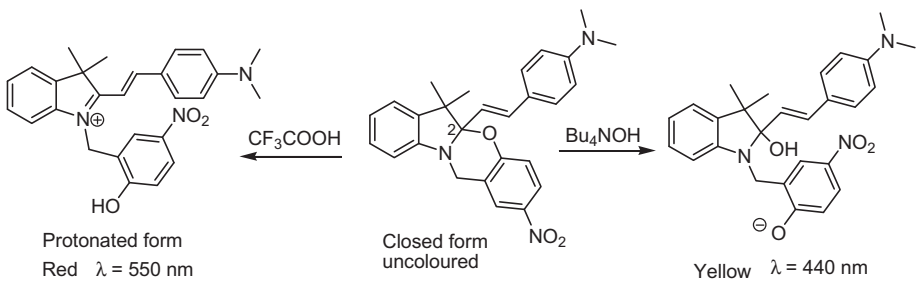
2. Results and discussion

A variety of substituted benzo[1,3]oxazines can be easily prepared by N-alkylation of 3,3-dimethyl-3*H*-indoles with 2-chloromethyl-4-nitrophenol in acetonitrile followed by spontaneous intramolecular oxazine cyclization [11]. Alternatively, the 2-methylbenzo[1,3]oxazine **1** can be condensed with aldehydes to produce oxazines with extended conjugation [3,7]. The reaction of 2-methylbenzo[1,3]oxazine **1** with 4-dimethylaminobenzaldehyde, in the presence of trifluoroacetic acid (0.30 eq) for 6 days in acetonitrile under reflux, is known to produce, after basic treatment with aqueous KOH solution, a photochromic oxazine with extended conjugation [3] (Scheme 3). Recently, Deniz et al. reported the synthesis of a series of oxazines using this methodology but without any basic treatment at the end. The reactions were carried out in CH_3CN or EtOH using even an excess of TFA. After solvent evaporation the residue was dissolved in CH_2Cl_2 and the addition of hexane or Et_2O caused the precipitation of the oxazines [7,12].

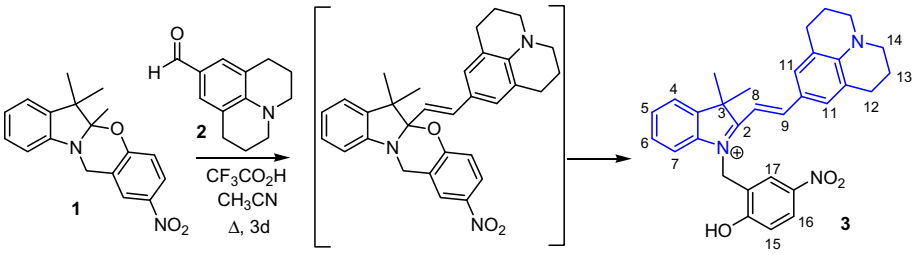
Following the same procedure, an acetonitrile solution of methyl oxazine **1**, julolidine-9-carbaldehyde **2** (1.0 eq) and CF_3COOH (1.0 eq) was heated at reflux. Within 3 h we observed the formation of a deep blue solution, from which a green crystalline precipitate started to form. After 3 days at reflux the precipitate was isolated by filtration (Scheme 4). The same result was observed when a catalytic amount of TFA (0.34 eq) was used.

Mass spectrometry (ESI-TOF) analysis of this solid indicated the molecular formula of the product as $C_{31}H_{32}N_3O_3$. The ^1H NMR spectrum (DMSO) of this compound showed all the expected aromatic signals for a benzo[1,3]oxazine but with an usual low field signal for the CH_2N protons at 5.68 ppm whereas in known benzo [1,3]oxazines these protons resonate around 4.4–4.7 ppm. The presence of a phenolic proton around 12.1 ppm and the absence of the expected ethylenic signals around 6 ppm were also noteworthy. In acetonitrile solution this compound shows a strong absorption at 591 nm ($\varepsilon = 1.8 \times 10^5\ M^{-1}\ cm^{-1}$), which resembles the ground state absorption of the model compound **4**, but no band at 440 nm, attributable to the 4-nitrophenolate was observed (Fig. 1). These results suggest the opening of the oxazine ring and the formation of a coloured polymethine indolium cation with an extended conjugation, linked to the uncoloured protonated phenolate **3**.

The structure of this new blue dye was unambiguously established using 2D NMR experiments. In particular ^1H–^1H scalar correlations were measured in COSY experiment (DMSO) between protons H-8 at 7.19 ppm and H-9 at 8.19 ppm with a coupling constant of 15.2 Hz and from H-4 (7.74 ppm) up to H-7 (7.49 ppm) via H-5 and H-6. The two aromatic julolidine protons H-11 appear as



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



Scheme 4. Synthesis of the blue dye **3**.

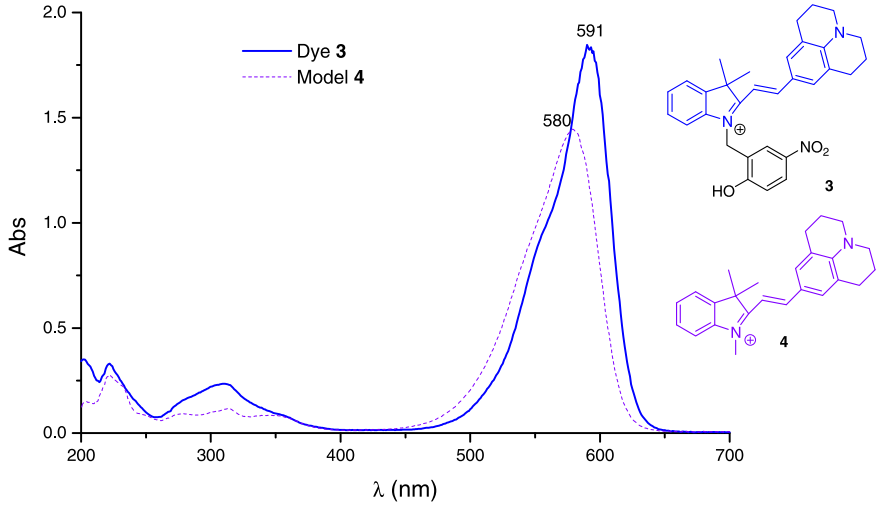


Fig. 1. Absorption spectra of the blue salt **3** and the model compound **4** in acetonitrile (1.0×10^{-5} M).

a very broad signal at 7.63 ppm at r.t. but became distinct from each other at 223 K in $CDCl_3$. The HMBC spectrum evidences significant long-range C–H correlations between carbon C-2 at 178.3 ppm and the CH_2N protons at 5.68 ppm, the $C(CH_3)_2$ methylenic protons at 1.76 ppm and H-9 at 8.19 ppm confirming the opening of the oxazine ring and the presence of the indolium cation. ^{19}F NMR spectroscopy confirmed the presence of trifluoroacetate as the counteranion in compound **3**. It is worth mentioning that the closed benzo[1,3]oxazines have a characteristic resonance around 102–106 ppm for the oxazine quiral carbon C-2 which, in this open form appears at 178.3 ppm, a value compatible with a positive charged 3*H*-indolium fragment.

To promote the closure of the oxazine ring in compound **3** we tried its reaction with bases. While refluxing an acetonitrile solution of **3** and NEt_3 (1 eq) led only to the decomposition of the starting material, when a $CHCl_3$ solution of the blue dye **3** was treated with an aqueous solution of KOH, at room temperature, the organic phase turned reddish and after work up the polar dye **5** was isolated.

The UV–Vis spectra of compound **5** showed two strong absorption bands in the visible spectrum, at 410 nm and 587 nm, which can be assigned to the phenolate anion and to the conjugated 3*H*-indolium cation respectively (Fig. 2). This suggests the formation of a stable ring opened zwitterionic form of the benzo[1,3] oxazine (Scheme 5). This hypothesis was confirmed by the ^1H NMR spectrum (in acetone-d6) of the dye **5** which showed similar resonances as the blue dye **3**. The main differences were an high field shift of almost all signals, in particular the CH_2N protons (from 5.60 to 4.86 ppm), protons H-8 (from 7.31 to 6.26 ppm) and H-9 (from 8.30 to 6.79 ppm), proton H-15 of the phenolic fragment (from 7.52 to 6.97 ppm) and the absence of any exchangeable protons, which are indicative of the presence of a phenolic anion in the structure (Fig. 3).

The change in the absorption spectrum between dyes **3** and **5** can be seen in Fig. 2. Addition of Bu_4NOH (10 eq) to the blue dye **3** leads to the decrease in the band at 591 nm and the rising of the band at 410 nm suggesting the presence of two chromophores: the phenolate anion and the conjugated 3*H*-indolium cation. This spectrum is identical to a sample of the zwitterionic compound **5**.

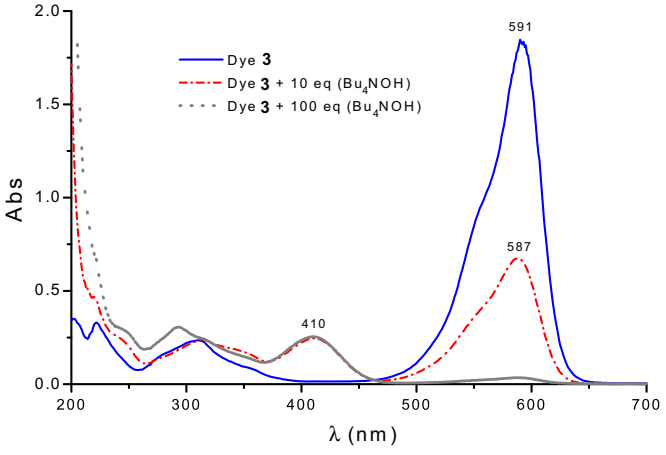
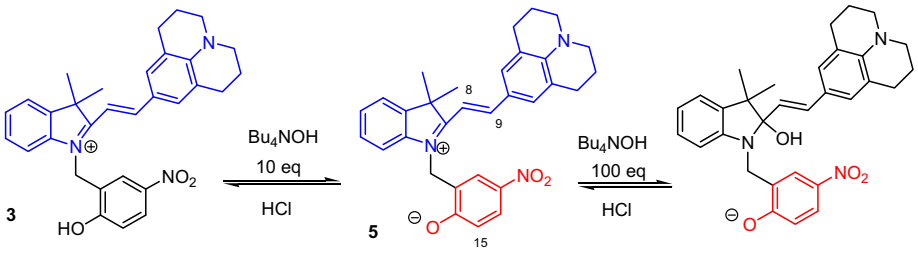


Fig. 2. UV–Vis spectra of dye **3** in acetonitrile (1.0×10^{-5} M) before and after addition of Bu_4NOH (10 and 100 eq).



Scheme 5. Acidochromism of dye **3**.

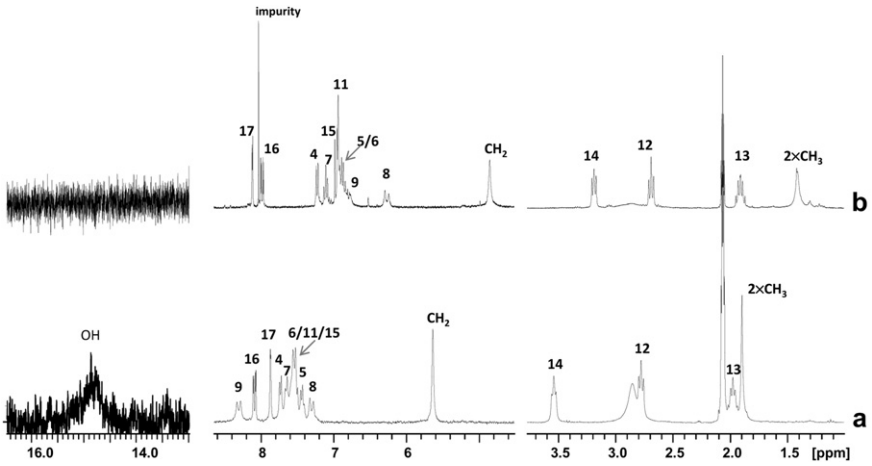


Fig. 3. ^{1}H spectra of (a) compound **3** and (b) compound **5** in acetone-d_6.

Addition of an excess of base (Bu_4NOH, 100 eq) lead to a yellow solution where the absorption at 591 nm nearly disappeared, indicating probably the formation of a coloured hemiaminal with only the phenolate chromophore. These transformations are reversible: addition of an excess of HCl leads to the disappearance of the phenolate band at 410 nm and the emerging of the band at 591 nm of compound **3** (Scheme 5).

These results indicate that dye **3** was probably formed by condensation of the starting 2-methylbenzo[1,3]oxazine **1** with julolidine-9-carbaldehyde, catalysed by the TFA acid, leading to an unstable closed benzo[1,3]oxazine, that spontaneously opens the oxazine ring leading to the open form **5** which under the action of the TFA and water, formed in the condensation, is converted to the dye **3**.

The fact that in diluted basic medium compound **5** does not cyclize back to the closed form, contrary to that observed with common benzo[1,3]oxazines [8,11], points towards an increased stability introduced by the julolidine residue. Studies on triarylmethane dyes, shows that the electron-donating ability of the julolidine moiety is stronger than the 4-(N,N-dimethylamino) phenyl group [13,14]. Julolidine dyes usually exhibit pronounced bathochromic shifts as well an increase of the absorption band intensity [15–18]. While in N,N-dimethylaniline the nitrogen atom has sp^3 hybridization, in the julolidine, due to the bridging by the methylene groups, the nitrogen exists preferentially in the sp^2 hybridization which permits a more efficient conjugation [19].

3. Conclusion

While the coloured ring opened forms of benzo[1,3]oxazines, obtained upon UV excitation, are thermally unstable and return to the uncoloured state in few ns, the introduction of a conjugated julolidine moiety in the structure lead to the overture of the oxazine ring with formation of a stable cationic blue dye with a conjugated 3*H*-indolium chromophore. Upon addition of base this dye is easily transformed into a zwitterionic compound with two chromophoric systems, absorbing at 410 and 587 nm, corresponding to a very stable opened form of the benzo[1,3]oxazine photochromic system, which is unable to undergo the intramolecular [1,3]oxazine ring closure.

4. Experimental

The reactions were monitored by thin-layer chromatography on aluminium plates coated with Merck silica gel 60 F_{254} (0.25 mm). Melting points were determined in open capillary tubes in a Buchi 530 melting point apparatus and are uncorrected. All compounds were characterized by NMR and MS. ^{1}H, ^{19}F and ^{13}C NMR and 2D NMR spectra were recorded at 298 K in $CDCl_3$, acetone-d_6 and DMSO-d_6 using a Bruker ARX400 spectrometer (at 400.13 and 100.62 MHz) or a Bruker Avance-500 MHz spectrometer. Heteronuclear ^{1}H–^{13}C HSQC and HMBC experiments were carried out using standard procedures. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. IR spectra were obtained on a Perkin–Elmer FTIR 1600 spectrometer using KBr pellets. Wavenumbers (ν_{max}) are reported in cm^{-1}. UV–Vis spectra were recorded on a CARY 50 Varian spectrophotometer in spectral grade acetonitrile. Low and high resolution electrospray ionization – time of flight mass spectra (TOF-ESI) were measured with an AutoSpecE spectrometer. All compounds were determined to be >95% pure by ^{1}H NMR spectroscopy. Julolidine-9-carbaldehyde [9], starting benzo[1,3]oxazine **1** [1] and model compound **4** [16] were prepared according to literature procedures.

4.1. 1-(2-Hydroxy-5-nitrobenzyl)-3,3-dimethyl-2-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[i,j] quinolizin-9-yl)vinyl]-3H-indolium trifluoroacetate **3**

A solution of 2-methylbenzo[1,3]oxazine **1** (0.30 g, 0.97 mmol), julolidine-9-carbaldehyde (0.20 g, 1.00 mmol) and CF_3CO_2H (0.074 mL, 0.97 mmol) in CH_3CN (20 mL) was refluxed for 3 days. The crystalline residue formed upon cooling was filtered off and washed consequently with cold CH_3CN (5 mL), i-PrOH (10 mL) and Et_2O (15 mL) to afford **3** as a deep green solid with a metal shining (0.33 g, 56%). Mp. 220–222 °C. IR: 593, 748, 808, 914, 1024, 1149, 1254, 1314, 1500, 1534, 1561, 1676, 2941. ^{1}H NMR (DMSO-d_6): 1.76 (s, 6H), 1.88–1.90 (m, 4H), 2.70–2.72 (m, 4H), 3.43–3.46 (m, 4H), 5.68 (s, 2H), 7.07 (d, J = 9.0 Hz, 1H), 7.19 (d, J = 15 Hz, 1H), 7.37 (t, J = 7.0 Hz, 1H), 7.41–7.49 (m, 3H), 7.63 (broad s, 2H), 7.74 (d, J = 7.0 Hz, 1H), 8.09–8.14 (m, 2H), 8.19 (d, J = 15 Hz, 1H). ^{13}C NMR (DMSO-d_6): 20.3, 26.7, 26.9, 43.5, 50.1, 102.7, 112.8, 115.9, 116.2, 118.2, 121.7, 121.9, 122.6, 124.5, 125.8, 126.3, 128.5, 139.4, 141.5, 141.7, 150.0, 153.7, 157.7, 157.9, 162.1, 177.8. ^{19}F NMR ($CDCl_3$): −73.4 (CF_3). HRMS (TOF ESI): calcd for $[C_{31}H_{32}N_3O_3]^+$ 494.2438; found: 494.2434. When 0.34 molar equivalents of TFA were used, the same crystalline solid was obtained in 43% yield.

4.2. 1,3,3-Trimethyl-2-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[3,2,1-ij] quinolizin-9-yl)vinyl]-3H-indolium perchlorate **4**

A solution of julolidine-9-carbaldehyde (0.15 g, 0.73 mmol) and 1,2,3,3-tetramethyl-3*H*-indolium perchlorate (0.20 g, 0.73 mmol) in 10 mL of freshly distilled acetic anhydride was heated at reflux for 5 min. The crystalline residue formed upon cooling to room temperature was filtered off, washed with EtOAc (10 mL) and diethyl ether (2 × 10 mL) to afford **4** (0.25 g, 75%) as a blue crystals with metallic shining. Mp. 239–242 °C (dec.) (lit. [16] 242 °C (dec.)). IR: 622, 701, 804, 1086, 1165, 1276, 1466, 1522, 1574, 2855, 2938. ^{1}H NMR (DMSO-d_6): 1.71 (s, 6H), 1.91 (m, 4H), 2.74 (m, 4H), 3.43 (m, 4H), 3.87 (s, 3H), 7.06 (d, J = 15 Hz, 1H), 7.41–7.42 (m, 1H), 7.49–7.51 (m, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.67 (broad s, 2H), 7.71 (t, J = 7 Hz, 1H), 8.13 (d, J = 15 Hz, 1H). MS (TOF-ESI) $(C_{25}H_{29}N_2)^+(ClO_4)^-$: 357 $(M)^+$, 342 $(M-CH_3)$.

4.3. 4-Nitro-2-(3,3-dimethyl-2-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[i,j]quinolizin-9-yl)vinyl]-3H-indolium)phenolate **5**

The trifluoroacetate 3*H*-indolium salt **3** (0.10 g, 0.18 mmol) was dissolved in $CHCl_3$ (75 mL). This solution was washed with aq. KOH (100 mL, 0.01 M) water (100 mL), dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure to afford the phenolate **5** (0.05 g, 61%) as a deep-blue solid. Mp. 147–149 °C (dec.). IR: 639, 748, 923, 1014, 1089, 1154, 1259, 1314, 1509, 1574, 2835, 2925. ^{1}H NMR (acetone-d_6): 1.42 (s, 6H), 1.91 (quintuplet, J = 6.1 Hz, 4H), 2.68 (t, J = 6.2 Hz, 4H), 3.19 (t, J = 5.7 Hz 4H), 4.86 (s, 2H), 6.27 (d, J = 15.6 Hz, 1H), 6.7–7.2 (m, 5H), 7.11 (t, J = 7.7 Hz, 1H), 7.22 (d, J = 7.2 Hz, 1H), 7.98 (dd, J = 9.1 Hz, J = 3.0 Hz, 1H), 8.11 (d, J = 2.8 Hz, 1H). ^{13}C NMR (acetone-d_6): 21.6, 23.4, 27.4, 40.3, 52.1, 109.0, 116.3, 117.5, 120.5, 121.0, 122.1, 123.6, 126.5, 127.4, 135.3, 137.6, 139.6, 140.2, 146.6, 160.3, 181.3. HRMS (TOF-ESI): calcd for $C_{31}H_{32}N_3O_3$: 494.2438 $[M + H]^+$; found: 494.2437.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2012.09.017.

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