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Indolinooxazolidine: A Versatile Switchable Unit

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ABSTRACT: The design of multiresponsive systems continues to arouse a lot of interest. In such multistate/multifunctional systems, it is possible to isomerize a molecular system from one metastable state to another by application of different stimulation such as light, heat, proton, or electron. In this context, some researches deal with the design of multimode switch where a same interconversion between two states could be induced by using indifferently two or more different kind of stimuli. Herein, we demonstrate that the association of an indolinooxazolidine moiety with a bithiophene unit allows the development of a new trimode switch. A reversible conversion between a colorless closed form and a colorful open form can be equally performed by light, proton, or electrical stimulation. In addition, the oxidation of this system allows the generation of a third metastable state.
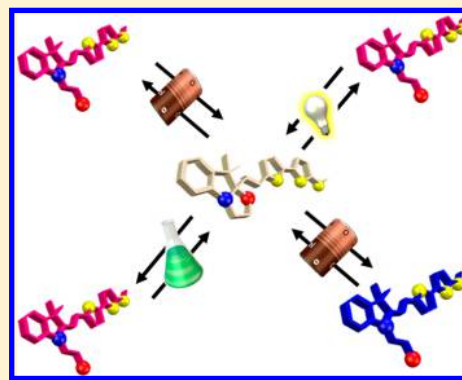
INTRODUCTION

Multiresponsive systems have attracted a lot of interest over the last few decades, due to their promising applications in the field of molecular logic gates.[1] These multistate/multifunctional systems can be defined as molecular systems that exist under several forms which can be interconverted by different external stimuli such as light, heat, proton, or electron.[2] To construct such systems, a common strategy involves the combination of different molecular switches connected through covalent links[1,3] or mixed within supramolecular assemblies.[4] For the development of such systems, the design and the preparation of bimodal switching molecules, which could be interconverted from one state to another by using indifferently two kinds of stimulation, for example, photon and electron, could create some interest. The most popular examples of bimodal switches are undoubtedly the diarylethene derivatives, which can exist under two thermally stable states: an open colorless form and a closed colored form. Their excellent photochromic behavior (fatigue resistance, short response time, high quantum yields, no thermal isomerization, ...)[5] has led to their application in many molecular systems which have been reviewed several times over the past decades.[5−9] In addition to these photochromic properties, Branda et al. show that some of them present also some interesting electrochromic behavior.[10] Later, Feringa's group studied in detail the oxidative electrochemical switching in dithienylcyclopentenes, which allows a switch between the open colorless form and the colored closed form by application of a redox potential.[11,12] Diarylethenes are not the only dual-mode photochromic compounds reported in the literature. In fact, the spiropyranes have also been extensively studied and largely used for the preparation of multiresponsive molecular system due to their solvato- and acidochromic properties[13−15] and also for their complexation abilities with some metal ions.[16−18] If the electrochromic behavior of some spiropyrans was reported[19−25] Feringa and Browne have reinvestigated the electrochemical behavior of the best known of them: the nitro-spiropyran.[26] They highlight that the electrochromic performances of these compounds result from the formation of a dimer through an irreversible oxidative aryl C−C coupling. Indeed, the presence of a methyl group in position 5 of the indoline moiety inhibits this dimerization and completely turns off the electrochromic properties as clearly demonstrated by the authors.

Reported in the nineties, the indolino[2,1-b]oxazolidine derivatives[27−29] are a more recent family of photochromic dyes. Associated with various styrylic residues, the indolinooxazolidine core could act as a multiaddressable switch displaying both photo- and acidochromic performances (Scheme 1). The opening of the oxazolidine ring could be reversibly and selectively achieved either under UV irradiation or acidity changes.[30]

From our point of view, the indolinooxazolidine core presents several options to introduce some chemical modifications either on the indoline moiety itself or on the extended π conjugate system by condensation with various aromatic aldehydes.[30,31] This versatility represents an opportunity to introduce several functional groups in order to elaborate more complicated molecular multistate systems.[32] Among the different possibilities, one of them is the introduction of a redox center, allowing the development of photo- and redox-active materials that are particularly attractive for applications in molecular memory or as a logic gate.[33−35]

Scheme 1. Photo- and Acidochromic Equilibrium of Several Indolinooxazolidine Analogues Used as Multiaddressable Switches in Nonlinear Optics[30]
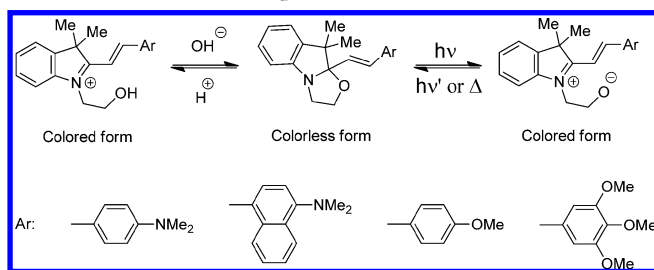
More interestingly, the presence of a redox center in the close vicinity of the photochromic unit can either suppress the photochromic behavior[36] or, on the contrary, enhance the stability of the photoproduct.[37] In this context, the present paper shows the design of a novel benzazoloxazolidine (BoX) derivative appropriately substituted by a redox center.

The application of specific potentials on this system induces ring-opening/closure, and combined with its acido- and photochemical properties, it demonstrates the trimodal switching function.

■ EXPERIMENTAL DETAILS

General Methods and Materials. Commercially available (Aldrich, Alfa Aesar, and abcr) chemicals were used as received. The catalyst Pd(PPh$_3$)$_4$ was synthesized according to a literature reference and stored under argon atmosphere in a refrigerator.[38] Diethyl ether (Et$_2$O) was freshly distilled from sodium each time prior to the reaction. Solvent (DME/water, 4:1) employed in Suzuki couplings was always degassed with argon prior to utilization. Organolithium reagent nBuLi (1.6 M in hexanes) were purchased from ACROS (AcroSeal) and were regularly standardized using diphenylacetic acid. For flash chromatography silica gel (Fluka, 60 Å pore size, 230−400 Å mesh) was used for all of the described compounds. For characterization NMR analysis was carried out using Bruker AVANCE 300 and Bruker AVANCE II 400 spectrometers in CDCl$_3$ at 25 °C. Chemical shifts are reported in ppm relative to the solvent (CDCl$_3$) residual value: δ = 7.26 for ^{1}H NMR, δ = 77.16 for ^{13}C NMR. Coupling constants are reported in Hz and rounded to the nearest 0.1 Hz. Where appropriate, HMQC, COSY, HMBC, and NOESY experiments were carried out to aid assignment. Mass spectra were acquired on a TOF mass spectrometer AccuTOF GCv by JEOL using an FD emitter (10 kV). Infrared spectra were recorded by using PerkinElmer Spectrum 100 spectrometer. Melting points were determined by using a Büchi melting point apparatus B-540. The synthesis procedure for the different compounds used in this study are reported below.

Oxazolidine 2a. A solution of 2-bromo-5-thiophenecarboxaldehyde (1.15 g, 6.0 mmol) and 2,3,3-trimethylindolino[1,2-b]oxazolidine 1a[39] (1.22 g, 6.0 mmol, 1.0 equiv) in EtOH (95 mL) was refluxed for 4 days. The solvent was removed under reduced pressure and the crude material was purified by flash column chromatography (PE/EtOAc, 95/5) to give the product 2a (1.3 g, 58%) as a yellow solid. R_f = 0.43 (PE/EtOAc, 9/1); mp =107−108 °C; ^{1}H NMR (400 MHz) δ = 1.16 (3H, s, CH$_3$), 1.44 (3H, s, CH$_3$), 3.45 (1H, dt, J = 8.3, 11.2, CH$_2$), 3.63 (1H, q, J = 7.4, CH$_2$), 3.66−3.71 (1H, m, CH$_2$), 3.79 (1H, dq, J = 3.2, 7.7, CH$_2$), 6.05 (1H, d, J = 15.7,

CH=CH), 6.76 (1H, d, J = 3.8, CH−Ar), 6.80 (1H, d, J = 7.8, CH−Ar), 6.90 (1H, d, J = 15.7, CH=CH), 6.95 (1H, d, J = 3.7, CH−Ar), 6.96 (1H, t, J = 7.4, CH−Ar), 7.14 (1H, d, J = 7.3, CH−Ar), 7.18 (1H, t, J = 7.5, CH−Ar); ^{13}C NMR (100 MHz) δ = 20.7 (CH$_3$), 28.7 (CH$_3$), 48.4 (C), 50.5 (CH$_2$), 63.9 (CH$_2$), 109.8 (C), 111.9 (C), 112.4 (CH−Ar), 122.2 (CH−Ar), 122.7 (CH−Ar), 125.4 (CH−Ar), 126.7 (CH−Ar), 126.9 (CH−Ar), 128.0 (CH−Ar), 130.7 (CH−Ar), 139.9 (C), 143.7 (C), 150.6 (C); IR $\overline{v}$ = 2964, 2879, 1477 cm^{-1}; MS (FD+) m/z (%) 378 (20) [M(^{81}Br) + H]$^+$, 377 (100) [M(^{81}Br)], 376 (20) [M(^{79}Br) + H]$^+$, 375 (100) [M(^{79}Br)]; HRMS (FD+) m/z calcd for C$_{18}$H$_{18}$BrNOS: 375.02925 [M(^{79}Br)], found 375.03005.

Oxazolidine 2b. A solution of 2-bromo-5-thiophenecarboxaldehyde (1.91 g, 10.0 mmol) and 1b[26] (2.17 g, 10.0 mmol, 1.0 equiv) in tBuOH (160 mL) was stirred at 95 °C in a sealed tube for 3 days. Then the solvent was removed and the crude material was dried under reduced pressure and purified by flash column chromatography (PE/EtOAc, 95/5) to give the oxazolidine 2b (2.72 g, 72%) as an orange solid. R_f = 0.61 (PE/EtOAc, 9/1); mp 120−122 °C; ^{1}H NMR (400 MHz) δ = 1.16 (3H, s, CH$_3$), 1.43 (3H, s, CH$_3$), 2.33 (3H, s, CH$_3$), 3.37−3.49 (1H, m, CH$_2$), 3.59−3.70 (2H, m, CH$_2$), 3.75−3.82 (1H, m, CH$_2$), 6.05 (1H, d, J = 15.7, CH=CH), 6.71 (1H, d, J = 7.9, CH−Ar), 6.76 (1H, d, J = 3.8, CH−Ar), 6.89 (1H, d, J = 15.7, CH=CH), 6.90 (1H, s, CH−Ar), 6.95 (1H, d, J = 3.8, CH−Ar), 6.99 (1H, d, J = 7.9, CH−Ar); ^{13}C NMR (100 MHz) δ = 20.6 (CH$_3$), 21.4 (CH$_3$), 28.7 (CH$_3$), 48.4 (C), 50.6 (CH$_2$), 64.0 (CH$_2$), 110.1 (C), 111.8 (C), 112.1 (CH−Ar), 123.4 (CH−Ar), 125.3 (CH−Ar), 126.8 (2 × CH−Ar), 128.5 (CH−Ar), 130.6 (CH−Ar), 131.6 (C), 140.0 (C), 143.7 (C), 148.3 (C); IR $\overline{v}$ = 2960, 2890, 1642, 1488 cm^{-1}; MS (FD+) m/z (%): 392 (15) [M(^{81}Br) + H]$^+$, 391 (100) [M(^{81}Br)], 390 (20) [M(^{79}Br) + H]$^+$, 389 (100) [M(^{79}Br)]; HRMS (FD+) m/z calcd for C$_{19}$H$_{20}$BrNOS 389.04490 [M(^{79}Br)], found 389.04349.

bTBoX 4a. To a solution of oxazolidine 2a (0.5 g, 1.33 mmol) in Et$_2$O (8 mL) was added nBuLi (1.6 M, 1.2 equiv) at −78 °C, and the mixture was stirred at the same temperature during 1.5 h. Then, B(OnBu$_3$) (0.54 mL, 1.99 mmol, 1.5 equiv) was added at once and the reaction mixture was stirred for 5 h at −78 °C. A solution of 2-bromo-5-(methylthio)thiophene[40] (0.83 g, 3.99 mmol, 3.0 equiv), Pd(PPh$_3$)$_4$ (0.15 g, 0.13 mmol, 0.1 equiv), ethylene glycol (2 drops) and 2 M Na$_2$CO$_3$ (2 mL) in Et$_2$O (20 mL) was stirred at room temperature for 15 min. Finally, the solution of in situ formed borate was added to the second solution and the reaction mixture was refluxed overnight. Water (15 mL) was added to the reaction mixture, and it was extracted with Et$_2$O (3 × 10 mL), dried (MgSO$_4$), concentrated under reduced pressure, and purified by flash column chromatography (PE/EtOAc, 95/5 → PE/EtOAc, 9/1) to give the product 4a (283 mg, 50%) as a yellow solid. R_f = 0.33 (PE/EtOAc, 9/1); mp 144−146 °C; ^{1}H NMR (400 MHz) δ = 1.19 (3H, s, CH$_3$), 1.45 (3H, s, CH$_3$), 2.53 (3H, s, CH$_3$), 3.43−3.52 (1H, m, CH$_2$), 3.60−3.73 (2H, m, CH$_2$), 3.77−3.84 (1H, m, CH$_2$), 6.11 (1H, d, J = 15.6, CH=CH), 6.81 (1H, d, J = 7.8, CH−Ar), 6.89−7.04 (6H, m), 7.09 (1H, d, J = 7.2, CH−Ar), 7.18 (1H, t, J = 7.6, CH−Ar); ^{13}C NMR (100 MHz) δ = 20.7 (CH$_3$), 22.4 (CH$_3$), 28.8 (CH$_3$), 48.4 (C), 50.5 (CH$_2$), 64.0 (CH$_2$), 110.0 (C), 112.4 (CH), 122.1 (CH), 122.7 (CH), 124.2 (2 × CH), 125.7 (CH), 126.4 (CH), 127.7 (CH), 128.0 (CH), 132.1 (CH), 136.5 (C), 137.0 (C), 139.7 (C), 140.0 (C), 141.1 (C), 150.8 (C); IR $\overline{v}$ = 2963, 2888, 1476 cm^{-1}; MS

Scheme 2. Synthetic route to 10-(2-(5′-(Methylthio)-2,2′-bithiophen)-5-yl)ethenyl)-indolino[2,1-b]oxazolidine Derivatives bTBoX (4a) and Me-bTBoX (4b)
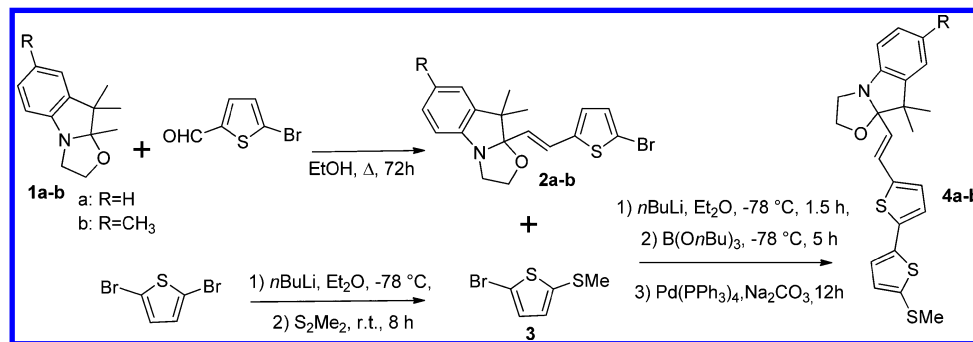
(FD+) m/z (%): 426 (25) [M + H]$^+$, 425 (100) [M]; HRMS (FD+) m/z calcd for $C_{23}H_{23}NOS_3$ 425.09418 [M], found 425.09348.

Me-bTBoX 4b. To a solution of oxazolidine **2b** (0.54 g, 1.43 mmol) in Et_2O (10 mL) was added nBuLi (1.6 M, 1.2 equiv) at −78 °C, and the mixture was stirred at the same temperature during 1.5 h. Then, borate (0.58 mL, 2.15 mmol, 1.5 equiv) was added at once and the reaction mixture was stirred for 3 h at −78 °C. A solution of 2-Bromo-5-(methylthio)thiophene (0.90 g, 4.30 mmol, 3.0 equiv), $Pd(PPh_3)_4$ (0.16 g, 0.14 mmol, 0.1 equiv), ethylene glycol (2 drops), and 2 M Na_2CO_3 (2 mL) in Et_2O (20 mL) was stirred at room temperature for 15 min. Finally, the solution of the borate was added to the second solution, and the reaction mixture was refluxed overnight. Water (15 mL) was added to the reaction mixture, and it was extracted with Et_2O (3 × 10 mL), dried ($MgSO_4$), concentrated under reduced pressure, and purified by flash column chromatography (PE/EtOAc, 98/2 → PE/EtOAc, 95/5) to give the product **4b** (271 mg, 43%) as a brown solid. R_f = 0.47 (PE/EtOAc, 9/1); mp: 155−157 °C; ^{1}H NMR (400 MHz) δ = 1.17 (3H, s, CH_3), 1.43 (3H, s, CH_3), 2.32 (3H, s, CH_3), 2.52 (3H, s, CH_3), 3.37−3.52 (1H, m, CH_2), 3.59−3.71 (2H, m, CH_2), 3.75−3.83 (1H, m, CH_2), 6.10 (1H, d, J = 15.6, CH=CH), 6.71 (1H, d, J = 7.9, CH−Ar), 6.89−7.03 (7H, m); ^{13}C NMR (100 MHz) δ = 20.6 (CH_3), 21.4 (CH_3), 22.6 (CH_3), 28.7 (CH_3), 48.4 (C), 50.8 (CH_2), 64.0 (CH_2), 110.2 (C), 112.1 (CH), 123.4 (CH), 124.2 (2 × CH), 125.6 (CH), 126.5 (CH), 127.6 (CH), 128.4 (CH), 131.5 (CH), 132.0 (C), 136.4 (C), 137.0 (C), 139.7 (C), 140.0 (C), 141.1 (C), 148.4 (C); IR $\overline{v}$ = 3409, 2960, 2918, 1658, 1489 cm^{-1}; MS (FD+) m/z (%): 440 (20) [M + H]$^+$, 439 (100) [M]; HRMS (FD+) m/z calcd for $C_{24}H_{25}NOS_3$ 439.10983 [M], found 439.10875.

Electrochemical Experiments. These were carried out with a Biologic SP-150 potentiostat driven by the EC-Lab software including ohmic drop compensation. Cyclic voltammetry (CV) was performed in a three-electrode cell controlled at a temperature of 293 K in a glovebox containing dry, oxygen-free (<1 ppm) argon. Working electrodes were platinum planar disk electrodes (o.d. = 2 mm). Counter electrodes were platinum wires. Reference electrodes were Ag/AgNO$_3$ (0.01 M CH_3CN). Experiments were recorded in dry HPLC-grade acetonitrile (CARLO ERBA) with tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, electrochemical grade, Fluka) as supporting electrolyte. All the potential reported were calibrated versus ferrocenium/ferrocene couple (Fc$^+$/Fc).[41] On the basis of repetitive measurements, absolute errors on potentials were found to be around ±5 mV.

Time-Resolved Spectroelectrochemistry. This was performed using the already described home self-made cell.[42] The body of the cell and all the parts are made of Teflon in order to be compatible with a broad variety of solvents. Viton O-rings are used where needed in order to ensure gas-tightness. The working electrode is a 2 mm diameter disk of polished platinum inserted in a Teflon rod. It is mounted in the central well on a micrometer screw that permits fine adjustment of the distance between the electrode and the optical window, while maintaining the surface of the electrode parallel to the window. A distance of 25−200 μm between the surface of the electrode and the optical window was typically used in our experiments. Electrochemical measurements were carried out using a platinum wire counter electrode and a silver wire as a quasireference electrode with a Biologic SP-150 potentiostat driven by the EC-Lab software including ohmic drop compensation. Experiments were recorded in dry HPLC-grade acetonitrile (CARLO ERBA) with tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, electrochemical grade, Fluka) as supporting electrolyte. All solutions were prepared and transferred into the spectroelectrochemical cell in a glovebox containing dry, oxygen-free (<1 ppm) argon, at room temperature. Spectrophotometric measurements were carried out with a homemade bench composed of different PRINCE-TON INSTRUMENTS modules (light sources, fibers, monochromators, spectroscopy camera and software). To start the two experiments at the same time, the two benches are synchronized with TTL signals.

■ RESULTS AND DISCUSSION

In that connection, we have synthesized two new BoX derivatives bearing a bithiophene (bT) as an aromatic substituent. The bT was selected for its well-known redox behavior[43] and easy synthetic access.[44] Indeed, the preparation of bTBoX (**4a**) and its methylated derivative, Me-bTBoX (**4b**) was straightforward. Condensation of conveniently susbtituted 2,3,3-trimethylindolino[2,1-b]oxazolidines and 5-bromo-2-thiophenecarboxaldehyde yielded the corresponding key intermediate (**2a−b**). Target molecules **4a** and **4b** were obtained by subsequent coupling reaction which allowed the extension of the π conjugate system as described on Scheme 2.

The incorporation of a bT unit on the indolinooxazolidine core does not affect its usual acidochromic properties. Upon acidity change, a large variation of the UV−visible spectrum is observed. As we can see in Figure 1, adding some acetic acid to a solution of bTBoX and Me-bTBoX in acetonitrile reveals a large absorption band centered at 523 nm with a concomitant decrease of the absorption at 360 nm. According to previous
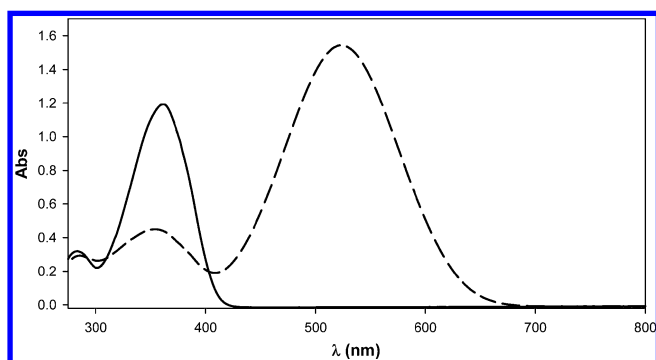
Figure 1. UV−visible absorption spectrum of btBoX in acetonitrile (0.2 mM) in absence (solid) and in the presence of acid (dashed).

studies,[30,45] this drastic spectral change is explained by the oxazolidine ring-opening which, on one hand increases the length of π-conjugated system and on the other hand, induces the generation of charge transfer between the electron donating thiomethyl susbtituent and the electron withdrawing indolenium moiety. The neutralization of the media by simple addition of any base (K$_2$CO$_3$ or NEt$_3$) induces the oxazolidine ring closure and allows us to recover the original spectrum.

Although acidochromic properties are not affected by the introduction of the bithiophene unit, the photochemical behavior of bTBoX and Me-bTBoX presents some differences in comparison with previously reported BoX derivatives. In these series, the photochromism is restricted to 254 nm whereas ring-opening was reported to be also efficient in the maximum absorption band (typically 280−360 nm)[27,30] and the observed rate is slower.[46] As expected for an interconversion between two isomers, some isosbestic points are observed (309 and 398 nm). Unfortunately, prolonged irradiation caused slight deviation of them which suggests the probability of decomposition of one or both forms. Furthermore, the photogenerated form shows thermal stability and no sign of thermal back-isomerization was detected even after few days. Water traces contained by acetonitrile induce the protonation and solvation of the photogenerated form leading to a protonated open form thus preventing a quantitative ring-

closure under visible irradiation. Bleaching has been temporally observed using a continuous laser emitting at 532 nm (±10 nm; 1 mW), but the system returns to the open form when the irradiation is stopped. Nevertheless, the back conversion of irradiated solutions, from open to closed form, can be carried out by addition of a base. At this moment, a total bleaching of the solution is observed restoring the initial spectrum (Figure 2).

As already reported, solvents play an important role toward the photochemical behavior of the BoX derivatives.[46] Since the 1970s, there have been numerous reports of the photosensitization of dechlorination reaction of chlorinated aromatics by aliphatic or aromatic dialkylamines such as triethylamine or N,N-dimethylaniline, due to a photoinduced electron transfer between them.[47−49] On the basis of this, addition of a small amount of chlorobenzene (10%) to our systems should increase the kinetics of their photoinduced responses. By following the coloration of the solution as a function of the irradiation time, it is possible to estimate the apparent kinetic constants in our experimental conditions. As suggested by our assumption, the presence of the chlo-robenzene increases the kinetic constant by almost a factor of 60 (0.24 and 14.6 s^{-1} without and with chlorobenzene respectively). Starting from this, it is reasonable to assign the large improvement of the oxazolidine ring-opening kinetic to the easiest generation of the BoX radical cation. This observation led us to believe that the same ring-opening/closure could be also achieved electrochemically. Therefore, we investigated the electrochemical properties of our BoX derivatives.

The electrochemical behavior of **4a** and **4b** were investigated in acetonitrile by cyclic voltammetry (CV). As shown on Figure 3, both compounds exhibit two successive oxidations, one being irreversible and the second reversible at 0.59 and 0.72 V vs Fc$^+$/Fc, respectively.

The localization of this first oxidation wave is not clear because it could occur either on the bithiophene or the indoline which are not conjugated.[31,45] The redox potential of various 5,5′-disubstituted bithiophenes was already reported close to 0.53 V vs Fc/Fc$^+$ when it is substituted by two thiomethyl groups.
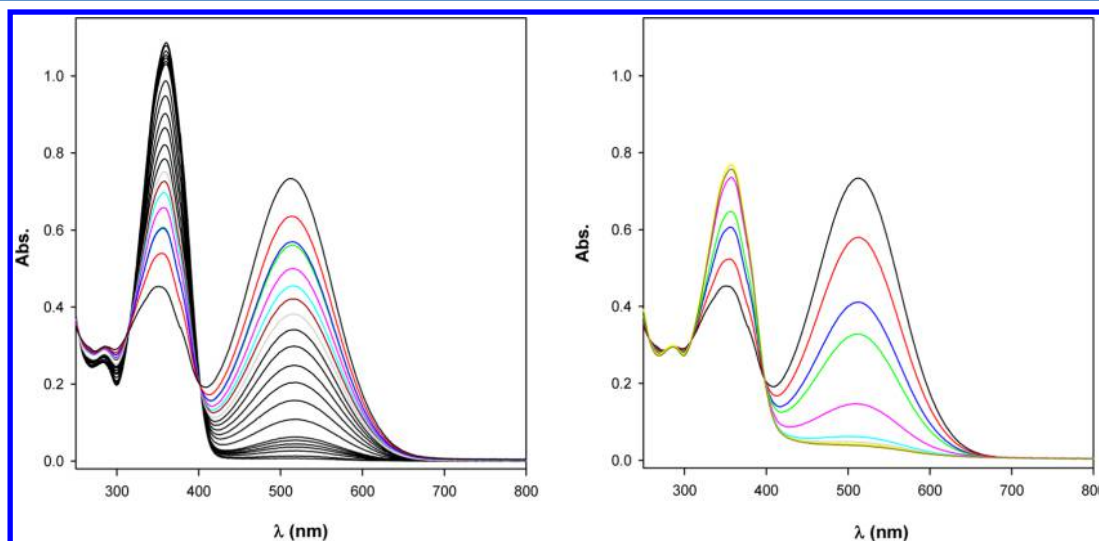

Figure 2. Evolution of the UV−visible absorption spectrum of **4a** in acetonitrile (0.2 mM) upon irradiation at λ_{irr} =254 nm (left) and its back conversion to closed form by NEt$_3$ addition (right).
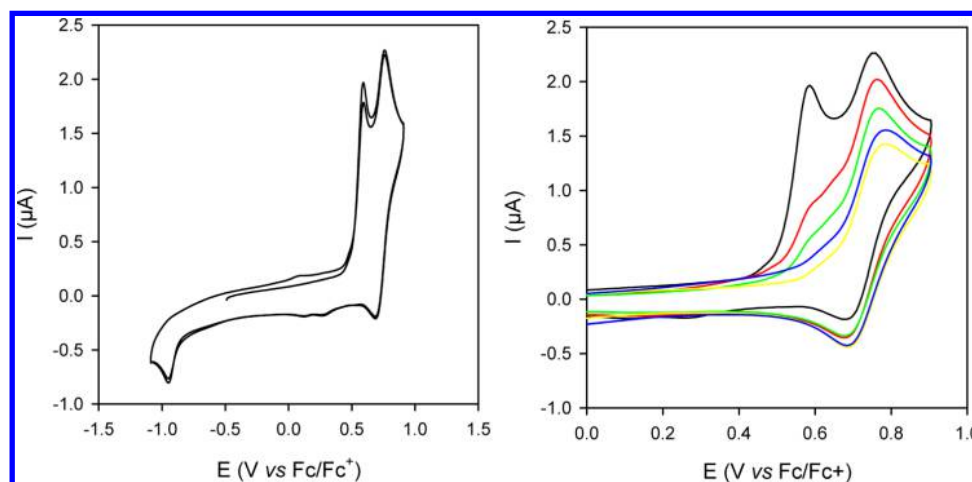
Figure 3. CV of **4a** in acetonitrile (0.2 mM) with (TBA)PF$_6$ (0.1 M) on Pt working electrode at 100 mV·s^{-1} (left). Evolution of CV of **4a** during the electrolysis of the solution at 0.6 V vs Fc$^+$/Fc (right).
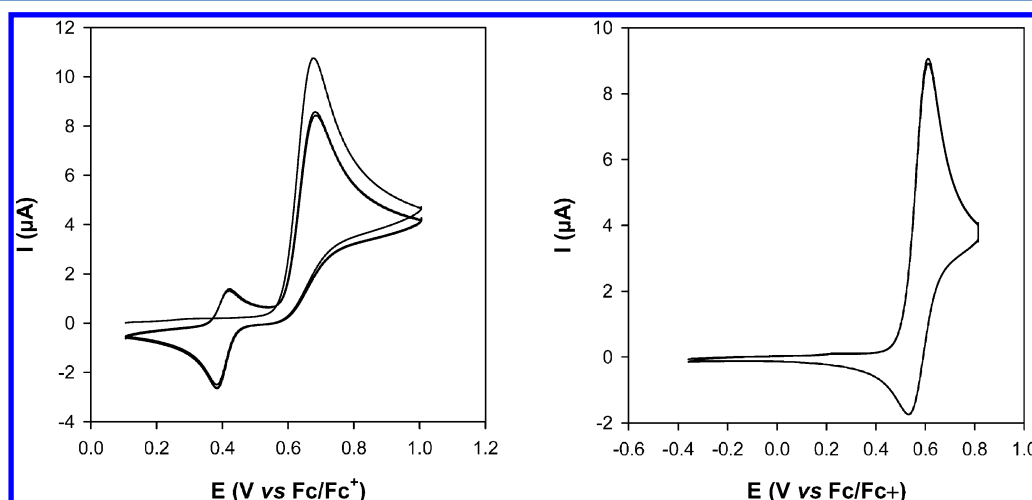

Figure 4. CV of **1a** (left) and **1b** (right) in acetonitrile (1 mM) with (TBA)PF$_6$ (0.1 M) on Pt working electrode at 100 mV·s^{-1}.

Because of the absence of electrochemical data reported on indolinooxazolidines, CV experiments were carried out on **1a** and **1b** (Figure 4). The derivatives **1a** and **1b** present two distinct electrochemical behaviors. The oxidation of the naked BoX, **1a**, close to 0.6 V vs Fc/Fc$^+$, is fully irreversible with the appearance of a new system at lower potential (0.4 V vs Fc/Fc$^+$). The irreversibility of this oxidation process can be explained by the possible dimerization of the radical via an aryl−aryl homocoupling in position 5 as observed for spiropyran derivatives.[26] The introduction of a methyl group in position 5 should avoid this dimerization. The oxidation of the Me-BoX, **1b**, slightly less than 0.6 V (due to the electron donating effect of the methyl group), does not produce a dimerization as predicted. Even if CVs of **1b** are fully reversible at high scan rate, an irreversibility of the radical cation can be observed below 200 mV·s^{-1}, suggesting its fast isomerization to a ring-open radical cation.

On the basis of these results, the spatial localization of the first oxidation of the dyads **4a** and **4b** is problematic, because the redox potentials of the two distinct parts of the derivatives (bithiophene, indoline) are very close.

Two facts, however, suggest an oxidation of the bithiophene unit: the oxidation potential of the dyad is not affected by the presence of the methyl in position 5 and the absence of any signal at ca. 0.4 V excludes a dimerization process.

Although, most 5,5′-disubstituted bithiophenes present a first reversible oxidation,[43,50] the reversibility is not observed at high scan rate. The stability of the radical cation is strongly affected by the presence of the indolinooxazolidine, leading to a conformational change or a chemical reaction. It comes down to the appearance of a new system at −0.95 V, which does not exist until the first oxidation system at 0.59 V is not reached. Among the possible reactions involving the radical cation, its isomerization leading to the ring-opening of the oxazolidine appears the most suitable. This assumption is supported by two observations. First, the extension of the conjugation and the generation of the indolinium form acting as an electron withdrawing group should affect strongly the redox potential of the molecule, shifting the oxidation potential of bT toward positive potentials and inducing the second oxidation wave at 0.72 V. Second, a total electrolysis of the solution at 0.6 V induces a total disappearance of the first process at 0.59 V accompanied by a strong coloration of the solution (Figure 3).

In order to confirm that the oxidation at 0.59 V induces the oxazolidine ring-opening, we have carried out some spectroelectrochemical experiments.

E

The variation of the absorption spectrum as a function of the potential is depicted in Figure 5. As expected, a drastic spectral
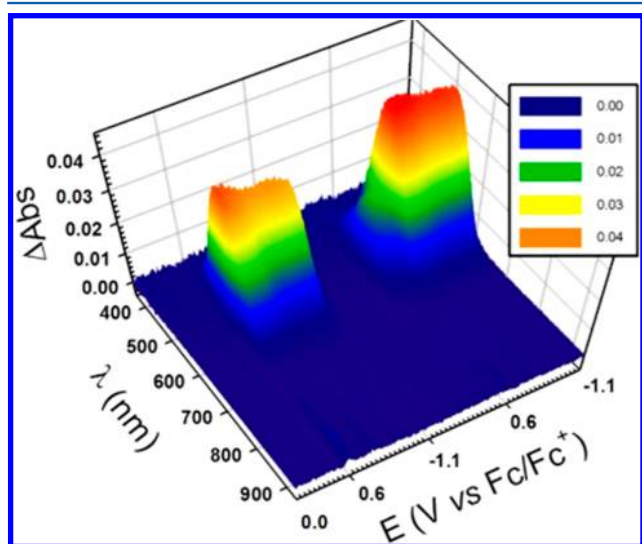

Figure 5. Spectroelectrochemistry in TLCV conditions (∼50 μm; 100 mV·s^{-1}) of BtBoX (0.2 mM) in acetonitrile with (TBA)PF$_6$ (0.1 M) as electrolyte on a platinum electrode.

change of the solution is observed at 0.59 V. A decomposition of the visible spectrum at this potential reveals the formation of three major bands at 534, 558, and 893 nm (Figure 6).

The first band is assigned to the open form by a simple comparison between electrolyzed and acidified solution. The presence of the two bands at 558 and 893 nm at 0.59 V could be assigned to the formation of a radical cation localized on the bithiophene as a transient species.

Indeed, stable radical cations from disubstitued bithiophene derivatives such as 5′-bis(methylthio)-2,2′-bithiophene are known to generate two absorption bands in the spectral range between 540 and 560 nm and 840−900 nm.[51,52] Moreover, these radical cations can lead to π dimers during the oxidation process,[43,52] or subsequent decomposition,[53] and thus explain the presence of the slight electrochemical signal at 0.2−0.3 V.

If the oxazolidine ring-opening by electrochemical way is established, the back reaction from open to closed form could also be achieved by electrochemistry. Indeed, the reduction at −0.95 V both restores the oxidation wave at 0.59 V (Figure 3a) and the UV−visible spectra of the original solution. Spectroelectrochemistry experiments carried out on beforehand UV-irradiated solutions (λ_{irr} = 254 nm) confirm this assumption by the observation of the disappearance of the spectral signature of the open form at 534 nm once the potential reaches −0.95 V (Figure 7). In addition, the total electrolysis at −1.0 V of this UV-irradiated solution induces its full discoloration and restores the UV−visible spectra of the nonirradiated solution

If the introduction of a bithiophene moiety as redox center have allowed to induce electrochemically the oxazolidine ring-opening/closure, it provides also a possibility to generate a third metastable state. Indeed, as we can see on the CV (Figure 3), both compounds present a second reversible oxidation process at 0.72 V. This second process is assigned to the reversible oxidation of the bithiophene unit under the open form. As expected, the generation of this oxidized state induces a strong variation of the visible spectrum as shown by the results of the spectro-electrochemistry experiments (Figure 8).

A decomposition of the visible spectrum at this potential allows the appearance of the formation of three major bands at 501, 581, and 626 nm and a weaker one at 924 nm (Figure 9).

The presence of the spectroscopic band around 900 nm[52] seems to translate the radical nature of this oxidized state and the large bathochromic shift of all the bands assigned to an extension of the π-conjugated system. However, the possibility for a such planar molecule to form some π-dimer does not allow us to assign without a doubt all the different bands to the open radical cation form and avoid the presence of its corresponding dimer and, by consequence, request further investigations.

■ CONCLUSION

To conclude, we have demonstrated that the association of an indolinooxazolidine unit with a bithiophene moiety as redox center allows us to obtain an interesting trimodal switch where the interconversion between the colorless closed form and a colored open form can be indifferently performed by light, proton or electrical stimulation. If the presence of the
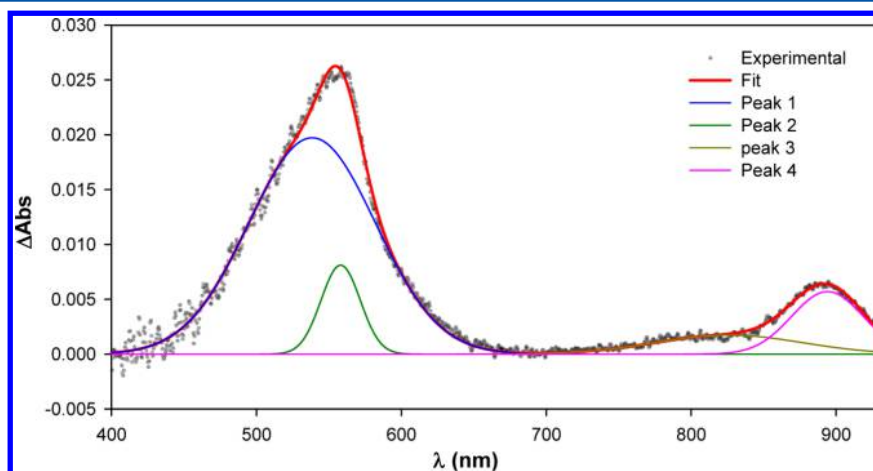

Figure 6. Variation of the UV−visible spectrum of **4a** in acetonitrile (0.21 mM) with (TBA)PF$_6$ (0.1 M) as electrolyte on a platinum electrode at 0.59 V.
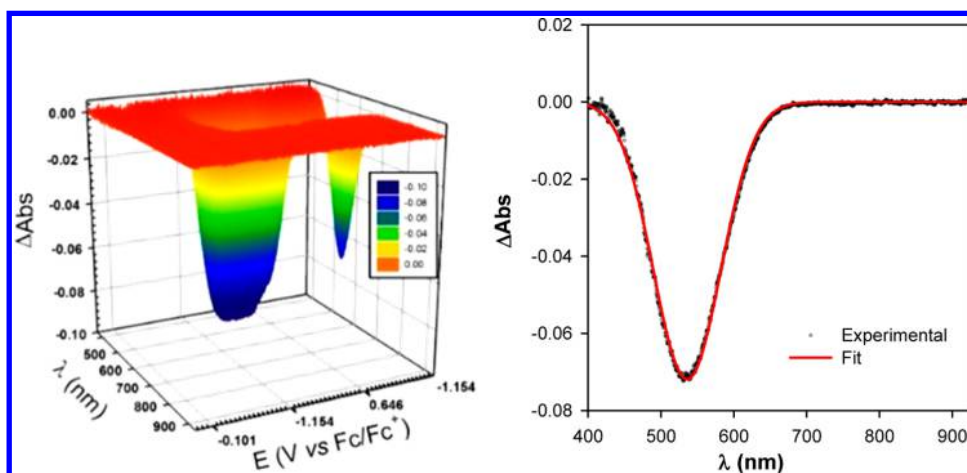
Figure 7. (left) Spectroelectrochemistry in TLCV conditions (~50 μm; 100 mV·s^{-1}) of irradiated BtBoX (0.2 mM) in acetonitrile with (TBA)PF$_6$ (0.1 M) as electrolyte on a platinum electrode. (right) Variation of UV−visible spectrum of an irradiated solution of **4a** in acetonitrile (0.21 mM) with (TBA)PF$_6$ (0.1 M) as electrolyte on a platinum electrode at −1.15 V.
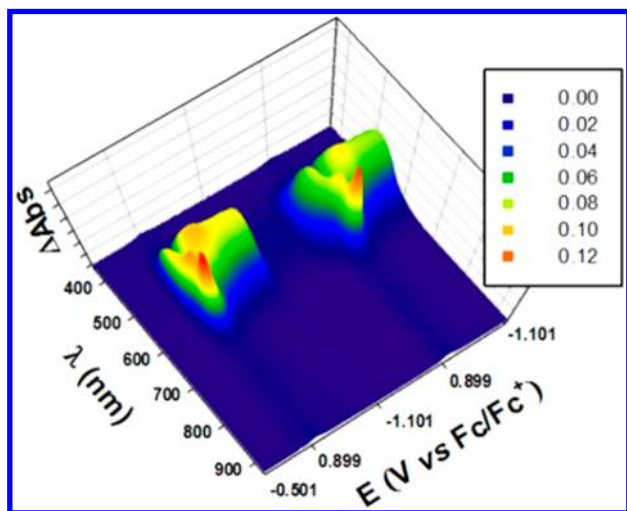

Figure 8. Spectro-electrochemistry under TLCV conditions (~50 μm; 100 mV·s^{-1}) of BtBoX (0.2 mM) in acetonitrile with TBAP (0.1 M) as electrolyte on a platinum electrode.

bithiophene did not affect the acido- and photochromic properties of the indolinooxazolidine, its oxidation to the corresponding radical cation conducts also to the opening of

the oxazolidine ring certainly by a delocalization of the radical from the bithiophene to the indolinooxazolidine. As consequence, we can propose that the electrochemical processes could be described as EC mechanisms with first the electrochemical generation of the radicals, and second, their chemical reorganizations (Scheme 3).

The electrochemical studies of the two benzazolooxazolidine derivatives prepared for this study, show that the open forms can be reversibly oxidized leading to a third metastable species. This oxidation is accompanied by a strong bathochromic shift (almost 100 nm) of the absorption maximum wavelength. Thus, an electrical stimulation can be used to switch the absorption maximum of the solution form a colorless solution (λ_{max} = 360 nm) to two different colored ones (λ_{max} = 534 or 626 nm) depending on potential applied (Scheme 4).

This possibility to specifically address these systems between three different states represents a way to tune their collective properties, in particular for nonlinear optic application where the indolinooxazolidine derivatives have shown a promising response.
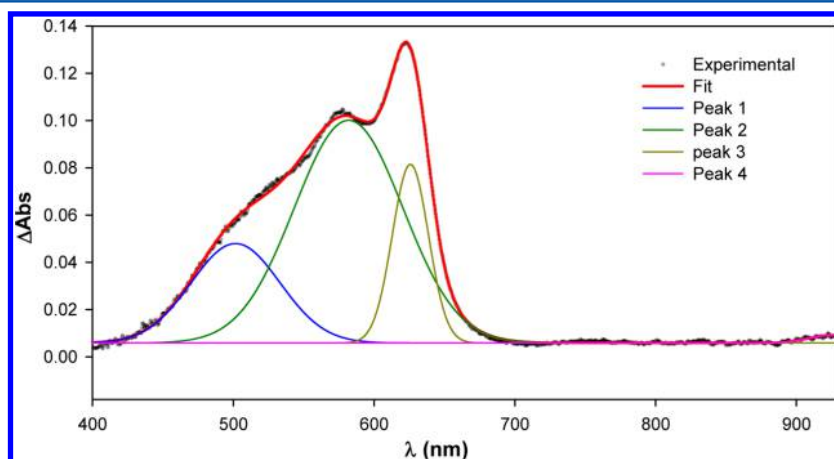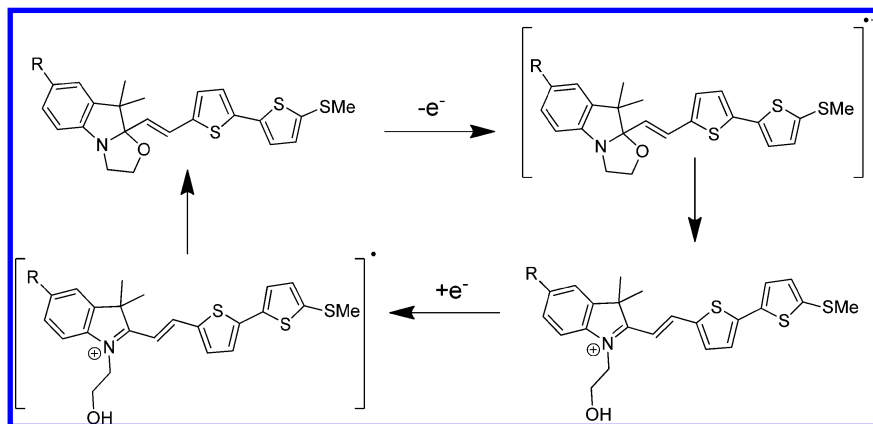

Figure 9. Variation of the visible spectrum of **4a** in acetonitrile (0.21 mM) with (TBA)PF$_6$ (0.1 M) as electrolyte on a platinum electrode at 0.81 V.

Scheme 3. Proposed Electrochemical Mechanism for the Reversible Interconversion of Benzazolooxazolidine between Their Open and Closed Forms

Scheme 4. Proposed Structure of the Three Metastable States of the Dyad Indolinooxazolidine–Bithiophene
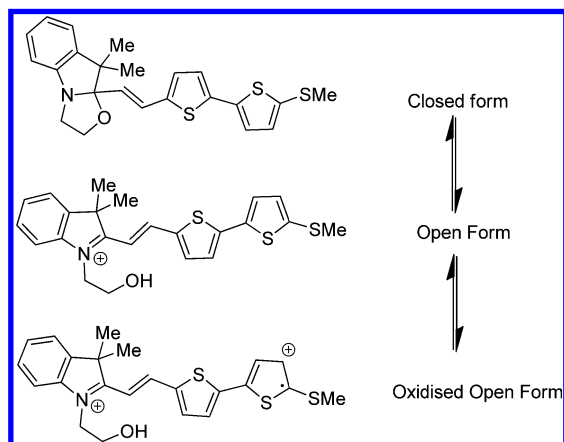
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Notes

The authors declare no competing financial interest.

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