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ABSTRACT

Keywords:
indolino[2,1-b]oxazolidine
Multi-responsive systems
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This work presents an original strategy to modulate the electrochemical properties of the indolino[2,1-b]oxazolidine core appropriately substituted in position 5 (para-substitution of the phenyl ring) by acceptor or donor groups (CHO, OMe, Me, F, H, Cl, Br). Supported by spectroelectrochemical experiments and confronted to electrochemical simulations, the stepwise oxidation of indolino[2,1-b]oxazolidine derivatives involves an electrochemical mechanism which depends on the para-substitution of the phenyl ring and leads to either the formation of a stable radical cation, the opening of the oxazolidine ring or an irreversible aryl C-C coupling.

1. Introduction

Multi-responsive systems have attracted a lot of interest since several years, due to their promising applications in the field of molecular logic gates [1]. These systems can be defined as molecular systems which exist under several forms presenting different properties which can be interconverted by using different external stimuli such as light, heat, chemical species, proton or electron [2]. In this context, numerous molecules, involving the combination of several molecular switches connected by covalent links, were designed in order to modulate their optical, photophysical, redox, or complexation behaviours [3].

Indolino[2,1-b]oxazolidine derivatives (BoX) are a recent family of photochromic dyes [4, 5] and associated with various styryl residues could act as a switch displaying photo-, acido- and recently electrochromic performances [6]. Indeed, the opening of the oxazolidine ring could be reversibly and selectively achieved either under UV irradiation, acidity changes or electro-oxidation, and conduct to the corresponding indoleninium [7].

If numerous studies report the electrochromic properties and electrochemical behavior of the spiropyranes which represent a Box analogue [8], to the best of our knowledge, and despite a real potential for electrochemical applications, only few works have been devoted to the specific design and fine electrochemical characterisations of indolino[2,1-b]oxazolidine derivatives [9]. This conclusion is also true for the indolino[2,1-b]oxazolidine core, that has not been extensively studied despite numerous options to introduce some chemical modifications either on indoline moiety itself or on pendant pi conjugated system, and that could modulate its properties.
In light of this situation, we propose to synthesize different indolino[2,1-b]oxazolidine derivatives appropriately substituted in position 5 (para substitution of the phenyl ring - Scheme 1) by different acceptor or donor groups (CHO, OMe, Me, F, H, Cl, Br) in order to study, by electrochemistry, spectroelectrochemistry and electrochemical simulations, the influence of these para substituents on redox properties.

2. Experimental section
2.1. Chemicals

General Experimental Conditions:
For purifications, technical grade silica gel (Aldrich, pore size 60 Å, 230-400 mesh, 40-63 µm) was used. For flash column chromatography, crystallizations and additional manipulations technical grade, non-dry solvents were used. Characterization of the isolated products was carried out in CDCl₃ or (CD₃)₂SO at 25 °C. Chemical shifts are reported in ppm relative to the solvent residual value: δ = 7.26 (CDCl₃), 2.50 ((CD₃)₂SO) for ¹H NMR and δ = 77.16 (CDCl₃), 39.52 ((CD₃)₂SO) for ¹³C NMR. Coupling constants are reported in Hz and rounded to the nearest 0.1 Hz. Where necessary, DEPT, HMQC, COSY, HMBC, experiments were carried out to aid assignments.


Synthesis of 5-Bis-(2,3,3-trimethylindolino[1,2-b]oxazoline) i.e (BoX-BoX):
To a solution of 5-Bromo-2,3,3-trimethylindolino[1,2-b]oxazoline (0.25 g, 0.89 mmol) in THF (12 mL) nBuLi (1.10 equiv.) was added at -78 °C and the solution was stirred at the same temperature during 45 minutes. After this time B(O)nBu₃ was added and the mixture was stirred at -78 °C during 1 hour, followed by 2 hours at room temperature. By the end of this time another solution was prepared by mixing bromo-2,3,3-trimethylindolino[1,2-b]oxazoline (0.25 g, 0.89 mmol, 1.0 equiv.), Pd(PPh₃)₄ (0.10 g, 0.09 mmol, 0.10 mmol), 2M Na₂CO₃ (1.7 mL) and 1 drop of ethylene glycol in THF(8.0 mL). This solution was then added to the previously prepared borate and the reaction was refluxed overnight. The solvent was removed under reduced pressure and the crude material was taken up in DCM. This solution was washed with water and brine, dried (MgSO₄), concentrated under reduced pressure and purified by flash column chromatography (Petroleum ether/EtOAc, 9/1) to give the product (104 mg, 29%) as a pink solid. m.p.: 156-157 °C; ¹H NMR (300 MHz) δ 1.22 (6H, s, CH₃), 1.40 (6H, s, CH₃), 1.47 (6H, s, CH₃), 3.51-3.65 (4H, m, CH₂), 3.68-3.91 (4H, m, CH₂), 6.78 (2H, d, J = 8.1, CH), 7.22 (2H, t, J = 1.6, CH), 7.31 (2H, ddd J = 8.1, 1.7, 1.1, CH); ¹³C NMR (75 MHz) δ 17.7 (CH₃), 21.0 (CH₃), 28.3 (CH₃), 47.2 (C), 50.3 (CH₃), 63.2 (CH₂), 109.4 (C), 112.2 (CH), 121.2 (CH), 126.4 (CH), 135.9 (C), 140.6 (C), 149.6 (C); IR ʋ = 2961, 2928, 2881 cm⁻¹; MS (ESI): m/z (%): 405 (100) [M+H]⁺; HRMS (ESI): m/z calcd. for C₂₆H₃₃N₂O₇: 405.2537 [M+H]⁺; found: 405.2539.

2.2. Instrumentation

Electrochemical experiments 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 glove box containing dry, oxygen-free (< 1 ppm) argon. Working
electrodes were glassy carbon planar disk electrodes (Ø = 3 mm). Counter electrodes were platinum wires. Reference electrodes were Ag/AgNO₃ (0.01 M CH₃CN). Experiments were recorded in dry HPLC-grade acetonitrile with tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, electrochemical grade, Fluka) as supporting electrolyte. All the potential reported were calibrated versus ferricinium/ferrocene couple (Fc⁺/Fc) (IUPAC Recommendation) [13]. Based on repetitive measurements, absolute errors on potentials were found to be around +/- 5 mV.

**Time-resolved spectroelectrochemistry** was performed using the already described home self-made cell [14-16]. 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 5 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 quasi-reference 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 with tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, electrochemical grade, Fluka) as supporting electrolyte. All solutions were prepared and transferred into the spectroelectrochemical cell in a glove box containing dry, oxygen-free (<1 ppm) argon, at room temperature. Spectrophotometric measurements were carried out with a homemade bench composed of different PRINCETON 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.

**Electrochemical simulations** were performed by an electrochemical simulation program (DigiElch 7™), under the same conditions as experiments. Many electrochemical and chemical parameters can be optimized, and this makes the accuracy and the convergence of the simulation highly dependent on the number of parameters to be optimized.

3. Results and discussion

3.1. Preliminary results

All compounds were investigated by cyclic voltammetry under the same conditions (0.1 M TBAPF₆ in CH₃CN, glassy carbon working electrode) and three distinct behaviours are clearly observed. First, CVs of the BoX substituted with OMe exhibit a quasi-reversible one-electron process at 0.1 mV.s⁻¹ (Figure 1a). Second, CVs of the BoX substituted with Me, F, Cl and CHO presents an irreversible oxidation wave at 0.1 mV.s⁻¹ (Figure 1a). Third, CVs of the BoX substituted with Br or H show an irreversible oxidation peak followed, in the reverse scan at lower potentials, by the emergence of a unique quasi-reversible wave at ~0.39 V (Figure 1b), ascribed to the reversible reduction of the product of the fast dimerization of radical cations [17].
3.2. BoXs substituted with OMe, Me, F, Cl and CHO

According to previous works [9], we can assume the ring opening of the BoX during oxidation, the kinetic rate of this opening being modulated by the substituents. The open BoX are stable in the range of potentials used and can be partially closed at a potential close to -0.9 V vs Fc+/Fc. The thermal ring-closure reaction kinetic of the BoX is frozen in our experimental conditions, leading a quasi-irreversible ring-opening reaction. The stepwise oxidation of each BoX can be described by an electrochemical mechanism with a first one-electron process coupled to an irreversible chemical reaction (EC_{irr} process - Scheme 2 and Figure 2). To estimate the forward rate constant (k_f) of the ring-opening reaction, a series of CVs was performed between 20 mV.s⁻¹ and 2000 mV.s⁻¹. An accurate estimate of k_f is easy to make because the reversibility and irreversibility of CVs were observed at low and high scan rates, respectively (Figure 2). To determine thermodynamic (E_0) and kinetic (k_f) parameters of scheme 2 from our experimental data, a non-linear regression strategy applied to multiple data files simultaneously was carried out from the electrochemical simulation program DigiElch 7™ (Table 1). First at all, standard potentials (E^0) are substituent dependent to reach a range of ~600 mV between BoX-CHO and BoX-OMe. As expected [18-22], a linear dependence between the electrophilic substituent constants (Brown-Okamoto constant σ_p for radical cations [23, 24]) and the redox potentials is observed (Figure 3), confirming the influence of the substituents on the electronic density of the electroactive center through the phenyl ring. Conversely, no clear trend of the forward rate constant (k_f) of the ring-opening reaction vs. σ_p was found, despite strong efforts.

To confirm the ring opening of the BoX during oxidation, time resolved spectrelectrochemical experiments (CVs and chronoamperometry experiments) were performed on all BoX derivatives (Figure 4). The oxidation of BoX-R leads to the formation of (BoX-R)^+, characterized by an absorption band between 450-480 nm depending of the substituent. This absorption band disappears with time (exponential decrease - Figure 4B and 4C) in order to produce an open BoX (i.e. no absorption band is observed between 350nm and 900nm as described by Raymo and al. [25]). The good agreement between the simulated concentration-time profiles and experimental data in thin layer conditions (Figure 4D) allows the assignment of the absorption band at 450 nm (Figure 4C) to the (BoX-R)^+.

3.3. BoXs substituted with H and Br

To support the assignment of the reversible wave observed in reverse scan at 0.39 V to the reduction of the dimer of radical cations, the BoX dimer (i.e. BoX-BoX) was synthetized (Scheme 1). As expected, CVs of BoX-BoX exhibit a unique oxidation wave characterized by two very closed one-electron processes, at the same potential as those observed with the BoX-H and BoX-Br (Figure 1). As previously mentioned with similar systems [22], these two systems can be simplified to a two-electrons process, allowing to estimate the redox potential of BoX-BoX to 0.39 V by fitting modelled CVs with experimental CVs.

In addition, time resolved spectrelectrochemical experiments, carried out on BoX-Br, BoX-H and BoX-BoX, show that the oxidations of the BoX-H, BoX-Br and BoX-BoX generate a large absorption band close to 500 nm, assigned to the oxidized dimer BoX-BoX^2+ (Figure 5). Note that the absorption band of radical cation of the BoX-BoX can be also observed at 750 nm during the reversible oxidation of the BoX-BoX (Figure 5), confirming that the oxidation of the BoX-BoX is not a pure two-electron process but composed of two successive and very close one-electron steps.
Contrary to the previous works of Feringa et al. [8] on spiropyran derivatives, the kinetic of the dimerization of the radical cation is competing with the one of the ring-opening reaction of the boxes (Scheme 2). Moreover, differences can be also explained by the fact that both BoX derivatives do not follow the same reaction pathway to yield dimer. Indeed, in the case of the BoX-Br, we can assume that just after the formation of the dimer (BoX-Br)_2^{2+}, there is release of Br_2 and formation of the oxidized dimer BoX-BoX^{2+}. In the case of BoX-H, and as the Feringa’s model proposes, we can assume that the formation of the dimer (BoX-H)_2^{2+} leads to release 2 H^+ and generates the neutral dimer BoX-BoX, which can oxidize immediately to (BoX-H)_2^{2+} at this high potential. Finally the release of H^+ could promote, in the vicinity of the electrode, a spontaneous opening of the BoX-H as shown in many studies [26-28].

According to these first results, the stepwise oxidation could be proposed in agreement with three one-electron processes and two or three charge-coupled chemical reactions (i.e. dimerization and ring-opening reactions) (Scheme 3). To validate this model, we performed a set of voltammograms by varying the scan rate (from 20 mV.s⁻¹ to 2000 mV.s⁻¹) and the concentration of the initial BoX derivatives (3 10⁻³ M, 3 10⁻⁴ M, 3 10⁻⁵ M), the dimerization efficiency being highly dependent on the latter parameter. The good agreement between experimental data and modelized CVs in a whole range of concentration and scan rate supports the model of the stepwise oxidation of BoX-Br and BoX-H (Figures 6 and 7 and Table 2). Concerning the BoX-Br derivative (Figure 6), an increase in the scan rate or a decrease in the concentration induces a slight return of the reversibility of the electrochemical system BoX-Br⁺/BoX-Br. We also observe that the dimerization reaction is more efficient than the ring-opening reaction. Concerning the BoX-H derivative (Figure 7), the trend is respected despite greater difficulty to adjust experimental CVs to the proposed model (many reactions and problems of stoichiometry). Nevertheless, the dimer formation is favoured and H⁺ formation during the dimerization induces, in the vicinity of the electrode, a local acidity change that reduces the concentration of BoX-H by rapid spontaneous opening.

Electrochemical simulations and multi-data fittings confirm that the fitted redox potentials (Table 2) of the BoX-Br⁺/BoX-Br and BoX-H⁺/BoX-H vs. Brown-Okamoto constant agree with the same trend of the other BoX derivatives (Figure 3). The global dimerization constant (k_d) for BoX-H is greater than the one of BoX-Br, and is in the same order of magnitude (kf > 10⁶) as that observed for different systems, such as dimerization of α-thiophenes [29, 30] or dithiafulvenes [22] and polymerizations of aniline [31], thiophenes [32, 33] or pyrroles [32, 34] derivatives. The simulated concentration-time profiles in thin layer conditions (Figure 5D) combined to the spectroelectrochemistry measurements show that the absorption bands at ~500 nm and above 750 nm are clearly assigned to the BoX-BoX^{2+}, and the oxidized BoX-BoX⁺, respectively.

4. Conclusions

This work presents original strategy to modulate the properties of the indolino[2,1-b]oxazolidine core appropriately substituted in position 5 (para-substitution of the phenyl ring) by acceptor or donor groups (CHO, OMe, Me, F, H, Cl, Br). These BoX derivatives were investigated with electrochemical and spectroelectrochemical characterisations. They show different behaviours upon oxidation and demonstrate the dependence of the nature of these groups on the BoX derivatives upon oxidation.

The redox potentials of BoX derivatives correlate with the Brown-Okamoto constants σ_p⁺ confirming the influence of the substituents on electronic density of the electroactive center through the phenyl ring.
The stepwise oxidation of BoX derivatives depends on the para-substitution of the phenyl ring. Indeed, BoX substituted with OMe exhibits a quasi-reversible one-electron process, BoX substituted with Me, F, Cl and CHO present an irreversible oxidation wave leading to the open form of the BoX core, and BoX substituted with Br or H show an irreversible oxidation peak followed, in the reverse scan at lower potentials, by the emergence of a unique reversible wave characteristic of the dimer BoX-BoX.

The results demonstrate the potential of the indolino[2,1-b]oxazolidine core in view of its integration into multi-responsive systems, the para substitution of the phenyl ring being an additional asset for the creation of new types of molecular switch.

Acknowledgments

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References


Tables

**Table 1.** Electrochemical parameters of BoX-R extracted* from a set of CVs with DigiElch 7\textsuperscript{TM}.

<table>
<thead>
<tr>
<th></th>
<th>BoX-MeO</th>
<th>BoX-Me</th>
<th>BoX-F</th>
<th>BoX-H</th>
<th>BoX-Cl</th>
<th>BoX-Br</th>
<th>BoX-CHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E^o_1$ (V vs Fc+/Fc)</td>
<td>0.42±0.02</td>
<td>0.57±0.02</td>
<td>0.70±0.02</td>
<td>0.64±0.04</td>
<td>0.74±0.02</td>
<td>0.75±0.03</td>
<td>0.97±0.02</td>
</tr>
<tr>
<td>$k_{f1}$ (s\textsuperscript{-1})</td>
<td>0.005±10%</td>
<td>0.440±10%</td>
<td>0.058±10%</td>
<td>0.700±30%</td>
<td>0.027±10%</td>
<td>0.090±20%</td>
<td>0.630±10%</td>
</tr>
<tr>
<td>$\sigma_p$+</td>
<td>-0.78</td>
<td>-0.31</td>
<td>-0.07</td>
<td>0.00</td>
<td>0.11</td>
<td>0.15</td>
<td>0.73</td>
</tr>
</tbody>
</table>

* Diffusion constants (D) of species between 1 $10^{-5}$ cm$^2$/s$^{-1}$ and 5 $10^{-5}$ cm$^2$/s$^{-1}$ and standard heterogeneous rate constants ($k_\text{s}$) between 2 $10^{-5}$ cm.s$^{-1}$ and 10 $10^{-5}$ cm.s$^{-1}$, were used to test the accuracy and convergence of these two parameters. Errors are estimated based on the spread of all experimental errors and errors of the fit. Parameters were extracted from simulations based on schemes 2 and 3.

**Table 2.** Electrochemical parameters of BoX-H and BoX-Br extracted* from a set of CVs with DigiElch 7\textsuperscript{TM}.

<table>
<thead>
<tr>
<th></th>
<th>$E^o_1$ (V vs Fc+/Fc)</th>
<th>$E^o_2$ (V vs Fc+/Fc)</th>
<th>$k_{f1}$ (s\textsuperscript{-1})</th>
<th>$k_{f2}$ (M$^{-1}$s$^{-1}$)</th>
<th>$k_{f3}$ (s\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>BoX-Br</td>
<td>0.75±0.03</td>
<td>0.39±0.02</td>
<td>0.09±20%</td>
<td>1900±20%</td>
<td>\textbf{10^4±30%}</td>
</tr>
<tr>
<td>BoX-H</td>
<td>0.64±0.04</td>
<td>0.39±0.02</td>
<td>0.70±30%</td>
<td>4 $10^5$±30%</td>
<td>\textbf{10^4±30%}</td>
</tr>
</tbody>
</table>

* Diffusion constants (D) of species between 1 $10^{-5}$ cm$^2$/s$^{-1}$ and 5 $10^{-5}$ cm$^2$/s$^{-1}$ and standard heterogeneous rate constants ($k_\text{s}$) between 2 $10^{-2}$ cm.s$^{-1}$ and 10 $10^{-2}$ cm.s$^{-1}$, were used to test the accuracy and convergence of these two parameters. Errors are estimated based on the spread of all experimental errors and errors of the fit. Parameters were extracted from approximate simulations based on schemes 3.
Scheme 1. BoX-R derivatives and BoX-BoX.

Scheme 2. EC_{el} mechanism involved for BoX substituted with OMe, Me, F, Cl and CHO. Inset, the mechanism used for numerical simulations. B refers to the BoX-R and Bo to the open BoX-R.
Scheme 3. Electrochemical mechanisms proposed for BoX-Br (top) and BoX-H (bottom). Insets, the mechanisms used for numerical simulations (stoichiometry is not perfectly equilibrated because DigiElch 7™ software does not manage stoichiometric coefficients different from unity). B refers to the BoX-R, Bo to the open BoX-R and BB to the BoX-BoX.
Figure 1. Cyclic voltammograms of the different BoX-R derivatives (10⁻³ M) in 0.1 M TBAPF₆/CH₂CN on glassy carbon (A=0.07 cm²) at 100 mV.s⁻¹. a) BoX-OMe (dark), BoX-Me (green), BoX-F (red), BoX-Cl (blue), BoX-CHO (pink), b) BoX-BoX (dark), BoX-H (blue), BoX-Br (red).
Figure 2. Black lines: Cyclic voltammograms of BoX-Me (top) and BoX-OMe (bottom) at different scan rates (left: 50 mV.s\(^{-1}\); middle: 200 mV.s\(^{-1}\); right: 1000 mV.s\(^{-1}\)) in 0.1 M TBAPF\(_6\)/CH\(_3\)CN on glassy carbon electrode at 10\(^{-3}\) M. Note that the baselines were subtracted on CVs. Red short-short line: electrochemical simulations performed from experiments (BoX-Me: \(E_0^1 = 0.57\) V, \(k_{\text{f1}} = 0.44\) s\(^{-1}\). BoX-OMe: \(E_0^1 = 0.42\) V, \(k_{\text{f1}} = 0.005\) s\(^{-1}\), \(\alpha = 0.5\), \(D = 10^{-5}\) cm\(^2\).s\(^{-1}\) and \(k_s = 0.01\) cm.s\(^{-1}\) for all BoX-R).
Figure 3. Linear correlation of the redox potential $E^0$ (V) with the Brown-Okamoto constant $\sigma^+$ for various substituents. Black circles: BoX-R derivatives leading to an open form. Red triangle: BoX-R derivatives leading to an open form and to a dimer. Errors are estimated based on the spread of all experimental errors and errors of the fit.
Figure 4. Spectroelectrochemistry experiments of BoX-F in 0.1 M TBAPF$_6$/CH$_3$CN on glassy carbon electrode in thin layer conditions (close to 50 µm) at 0.8 V and 293 K. (A) Potential applied and current vs time representation. (B) 3D representation (wavelength, time) vs (absorbance). (C) Absorbance representation vs time at 450 nm (D) Concentration-time profiles of each simulated species in the thin layer (50 µm) calculated from electrochemical simulations.
Figure 5. Spectroelectrochemistry experiments of BoX-BoX (top) and BoX-H (bottom) in 0.1 M TBAPF$_6$/CH$_3$CN on glassy carbon electrode in thin layer conditions (close to 50 µm) at 10 mV.s$^{-1}$ and 293 K. (A) CV in current vs time representation. (B) 3D representation (wavelength, time) vs (absorbance). (C) Absorbance zoom of the 3D representation (D) concentration-time profiles of each simulated species in the thin layer (50 µm) calculated from electrochemical simulations of Figure 5 and 6.
Figure 6. Black lines: Cyclic voltammograms of BoX-Br at different concentrations (top: $3.5 \times 10^{-3}$ M; bottom: $3.5 \times 10^{-4}$ M) and at different scan rates (left: 50 mV.s$^{-1}$; middle: 200 mV.s$^{-1}$; right: 1000 mV.s$^{-1}$) in 0.1 M TBAPF$_6$/CH$_3$CN on glassy carbon electrode. Note that the baselines were subtracted on CVs. Red short-short line: electrochemical simulations performed from experiments: $E_1^0 = 0.75$ V, $E_2^0 = 0.39$ V, $k_f1 = 0.09$ s$^{-1}$, $k_f2 = 1900$ M$^{-1}$s$^{-1}$, $\alpha = 0.5$, $D = 10^{-5}$ cm$^2$.s$^{-1}$ and $k_s = 0.01$ cm.s$^{-1}$. 

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Figure 7. Black lines: Cyclic voltammograms of BoX-H at different concentrations (top: 3.5 $10^{-3}$ M; bottom: 3.5 $10^{-4}$ M) and at different scan rates (left: 50 mV.s$^{-1}$; middle: 200 mV.s$^{-1}$; right: 1000 mV.s$^{-1}$) in 0.1 M TBAPF$_6$/CH$_3$CN on glassy carbon electrode. Note that the baselines were subtracted on CVs. Red short-short line: electrochemical simulations performed from experiments: $E_0^1$ = 0.64 V, $E_0^2$ = 0.39 V, $k_1$ = 0.7 s$^{-1}$, $k_2 = 4 \cdot 10^5$ M$^{-1}$s$^{-1}$, $k_3 = 1 \cdot 10^4$ s$^{-1}$, $\alpha = 0.5$, $D = 10^{-5}$ cm$^2$.s$^{-1}$ and $k_s = 0.01$ cm.s$^{-1}$. Simulated CVs were calculated with an approximate simulation based on scheme 3.
Highlights

- Original strategy to modulate the electrochemical properties of the indolino[2,1-b]oxazolidine core.
- Study of the stepwise oxidation via cyclic voltammetry and spectroelectrochemistry.
- Confirmation of oxidation process by electrochemical simulations.