The study of the electrochemical properties of new electrochromic compounds based on 3-aryl-4, 5-bis (pyridin-4-yl) isoxazoles derivatives.

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Abstract. Electrochemical and optical properties of a new class of electrochromic 3-aryl-4,5-bis (pyridin-4-yl)isoxazoles derivatives containing conjugated pyridine fragments were investigated comparing with their precursor 1,2-bis(4-pyridinyl)ethylene derivative. Electrochromic cells based on synthesized substances were reversibly colored in brown upon the application of a voltage of 1.5 V.

1. Introduction
Electrochromic materials draw attention of researchers of different fields because of the possibility to construct from them a wide range of devices with low power consumption: units of information imaging [1-4], "smart" windows [5-9], antiglare mirrors for automobiles [10-11], "chameleon" type materials [12-13], chemical sensors [14], molecular machines, and organic current sources [15].

Based on conjugated pyridine derivatives, full-color RGB devices have been created [15-18], but the range of such developments is rather narrow. Broad variety of colors of electrochromic materials is still required, determining the search for new functional molecules with well-defined characteristics.

Earlier we have developed a method of new electrochromic derivatives of 3-aryl-4,5-bis(pyridin-4-yl)oxazole preparation [19].

Here we describe electrochemical and optical properties of a broadened series of electrochromic bis(pyridin-4-yl)oxazoles in comparison with that of their precursor 4,4-(ethene-1,2-diyl)bis(1-butyl)pyridinium) hexafluorophosphate.

2. Synthesis of electrochromes
Synthesis of the 3-aryl-4,5-bis(pyridin-4-yl)isoxazoles derivatives are shown at the Scheme 1. All procedures were made according to [19]. Two paths of synthesis were examined. The method using alkenes 1 seems to be more useful taking into account better accessibility of such compounds. On the other hand derivative 5b was only possible to obtain by cycloaddition of alkyne 4 to nitrile oxide 2a.
3. Electrochromic device
Electrochromic devices were created on the basis of synthesized electrochromes 5 using ITO electrodes on a flexible PET substrate. The electrolyte solution contained: 30 mmol of substance (1c and 5), 10 mmol of ferrocene and 20 mmol of tetrabutylammonium hexafluorophosphate dissolved in anhydrous propylene carbonate. When a voltage of 1.5 V was applied, compounds 5 and 1c were reversibly colored brown and red respectively.

4. Electrochemical properties
By analogy to viologens [20], we assume that the formation of resonance-stabilized radical cation 6 is a reason for the appearance of coloration of the cells upon voltage application, as shown in Scheme 2. In this case, two-electron reduction with an increased voltage leads to the formation of structure 7.

Scheme 2. Oxidation and reduction transitions for 3-aryl-4, 5-bis (pyridin-4-yl) isoxazoles derivatives.
The electrochemical behavior of the substances was studied by cyclic voltammetry (CV) in acetonitrile solution containing 0.1 M electrolyte LiClO$_4$. The three-electrode electrochemical cell consisted of a glassy carbon working electrode, a platinum counter electrode, and an Ag / AgCl pair in a saturated KCl solution as a reference electrode.

Table 1. The values of the potential peaks of reduction and oxidation.

| Electrochrome | $E_{\text{Red}}, \text{mV}$ | $E_{\text{Ox}}, \text{mV}$ |
|---------------|-----------------------------|-----------------------------|
| 1c            | -583.5                      | -362.7                      |
|               | -836.5                      | -627.0                      |
| 5a            | -650.5                      | -543.3                      |
|               | -835.0                      | -794.2                      |
| 5b            | -661.6                      | -557.4                      |
|               | -857.2                      | -784.9                      |
| 5c            | -680.3                      | -585.5                      |
|               | -901.1                      | -791.8                      |
| 5d            | -692.6                      | -586.9                      |
|               | -888.3                      | -777.9                      |
| 5e            | -637.4                      | -513.2                      |
|               | -844.2                      | -726.7                      |
| 5f            | -624.8                      | -529.3                      |
|               | -819.5                      | -713.9                      |

The electrochemical behavior of the new electrochromes 5a–f is similar with that of the known electrochromic compounds having two reversible peaks on the CV curve. CV curves of compounds 1c, 5a–f in 0.1 M LiClO$_4$/MeCN are shown at the Figure 1.

Data on electrochemical potentials of compounds 1c and 5 are presented in Table 1. First reduction peaks of compounds 5 lie from -624 to -692 mV and second from -819 to 901 mV. First oxidation peaks lie from -513 to 587 mV and second from 713 to 794 mV. Compound 1c is characterized by close reduction potentials but has much lower oxidation potentials.

A decrease in the potential value is observed during the transition from the acceptor dichlorophenyl (5e–f) to mesityl (5a–b) and then to donor trimethoxyphenyl (5c–d) substituents in the isoxazole fragment. The degree of influence however is quite low as evidenced by the potential difference between the corresponding oxidative and reduction transitions not exceeding 90 mV. The smallest difference in current between the first and the 30th cycle (Figure 1) is to be noted for compound 5c which allows us to suggest that this compound will be the most stable in this series.

Figure 2 represents changes in time in optical density of compound 1c and 5d which is typical for all compounds 5. It can be seen that plot for 1c has growing absorption band from 460 to 550 nm whereas plot for 5d 410 to 510 nm. However compound 1c has clear peak at 510 nm while 5d has broadened absorption area with no clear peak.
5. Conclusions

Thus, the electrochemical properties of the synthesized derivatives of 3-aryl-4,5-bis(pyridin-4-yl)isoxazoles in comparison with their precursor 4,4′-(ethene-1,2-diyl)bis(1-butylpyridinium) hexafluorophosphate were studied by CVA as well as optical changes at applied voltage in time. CVA data showed
Figure 2. Changes in the optical density of electrochromic cells based on compounds 1c and 5d in time at a permanent applied voltage of 2 V. The spectra were recorded in a range of 0-1.6 s with the interval between measurements 0.2 s.

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