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# Comparison of FT Raman spectra of some 5-nitroquinoxalines and their electropolymers

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## Abstract

FT Raman spectroscopy was used to characterize a set of five newly synthesized 5-nitroquinoxaline derivatives 2,3-disubstituted with 2-pyrrolyl, 2-furyl, 2-thienyl, phenyl and 2-pyridyl groups. Afterwards the 5-nitroquinoxalines were electrochemically reduced to 5-aminoquinoxalines and electropolymerized as films on the Pt electrode coated with porous Au. Comparing the SERS spectra of polymers with the Raman spectra of monomers, a mechanism of polymerization has been suggested. Specific spectral and electrochemical properties of films based on pyrrole substituted 5-aminoquinoxaline were verified by electropolymerization of 2,3-dipyrrol-2'-yl-5-nitroquinoxaline without a reduction step. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** FT-Raman spectroscopy; SERS; Electropolymerization; Surface films

## 1. Introduction

A wide range of species with the ability to recognize and sense anions was proposed in last few years (e.g. sapphyrins, cyclodextrines) [1]. Black et al. [2] have tested an ability of 2,3-dipyrrol-2'-yl quinoxaline and its derivatives to coordinate  $F^-$ ,  $Cl^-$ ,  $H_2PO_4^-$ . A set of five 5-nitroquinoxaline derivatives 2,3-disubstituted with 2-pyrrolyl, 2-furyl, 2-thienyl, phenyl and 2-pyridyl groups (Fig. 1) has been newly synthesized to test their capabilities of recognizing and sensing anions. This study is focused on the FT Raman spectroscopic analysis of these compounds and their electrochemically reduced 5-aminoquinoxaline derivatives polymerized on a gilded Pt electrode (a

Pt electrode coated with gold [3]) to form polymer films. The surface films were characterized by FT SERS spectra prior to test potentiometric responses to various anions [4].

## 2. Experimental

### 2.1. Materials

The set of five 2,3-disubstituted 5-nitroquinoxaline derivatives was prepared according a procedure described in Ref. [2]. All chemicals used were of analytical grade.

### 2.2. Instrumentation

FT Raman spectra were collected using a FT-NIR spectrometer Equinox 55/S (Bruker) equipped with Raman module FRA 106/S (Bruker). Samples

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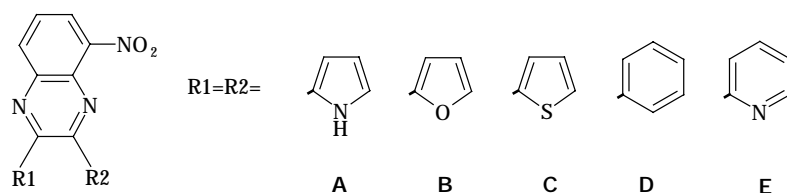


Fig. 1. Structures of 5-nitroquinoxaline derivatives 2,3-disubstituted with: (A) 2-pyrrolyl; (B) 2-furyl; (C) 2-thienyl; (D) phenyl; and (E) 2-pyridyl groups.

of 5-nitroquinoxaline derivatives and electropolymerized films were irradiated by the focused beam of Nd-YAG laser (1064 nm, Coherent) with power 80 and 15 mW, respectively. The scattered light was collected in backscattering geometry. Accumulated 256 and 512 interferograms were

processed to obtain Raman spectra with 2 and 4  $\text{cm}^{-1}$  resolutions of 5-nitroquinoxaline derivatives and of polymerized films, respectively. Two spectra were measured for every compound; five spectra were collected in different parts of any polymeric film.

Table 1

Wavenumbers ( $\text{cm}^{-1}$ ) of selected bands (characteristic bands of individual 2,3-substituents are given in *italics*, bands assigned to stretching vibrations of  $\text{NO}_2$  [5,8] are underlined) observed in the FT Raman spectra of 2,3-disubstituted 5-nitroquinoxalines in ranges 3200–2950, 1650–1300 and 1300–800  $\text{cm}^{-1}$

Pyrrolyl	Thienyl	Furyl	Pyridyl	Phenyl	Average value <sup>a</sup>	Average value <sup>a</sup> of some 5-substituted quinoxalines [7]
<i>3141 w</i>		<i>3154 m</i>				
<i>3133 m</i>		<i>3139 w</i>				
<i>3119 m</i>	<i>3111 m</i>	<i>3115 w</i>				
<i>3103 m</i>	<i>3085 m</i>			<i>3085 w</i>		
	<i>3073 w</i>		<i>3073 m</i>	<i>3070 sh</i>		
3064 m	3062 w	3068 m	3062 m	3064 m	3064	
			<i>3053 sh</i>	<i>3044 w</i>		
			<i>3037 w</i>	<i>3028 w</i>		
1615 w	1615 w	1596 w	1615 w	1617 w	1612	1614
<i>1571 w</i>		<i>1568 s</i>	<i>1592 s</i>	<i>1598 s</i>		
<i>1549 m-s</i>			<i>1571 m-s</i>	<i>1581 w</i>		
1556 sh	1554 w	1541 sh	1554 m	1554 w	1552	
<u>1536 m</u>	<u>1537 m</u>	<u>1535 m</u>	<u>1530 w</u>	<u>1543 m</u>	<u>1536</u>	
<i>1524 m</i>	<i>1524 m</i>					
		<i>1484 s</i>		<i>1498 m</i>		
			<i>1475 m</i>			
<i>1424 m</i>	<i>1428 s</i>		<i>1442 s</i>			
	<i>1418 s</i>					
1390 vs	1393 vs	1400 vs	1394 vs	1397 vs	1395	1383
	<i>1348 m</i>	<i>1381 w</i>				
<u>1343 m</u>	<u>1331 m</u>	<u>1338 m</u>	<u>1341 m</u>	<u>1331 m</u>	<u>1337</u>	
1249 m	1243 w	1244 sh	1245 m	1245 m	1245	1240
1153 w	1148 w	1148 w	1152 w	1147 w	1150	1153
1072 w	1065 w	1069 w	1065 w	1067 w	1068	1068
852 w	862 m	854 w	871 w	858 w	859	863
826 w	828 w	821 w	837 w	838 w	830	828
808 m	806 m	804 m	815 m	811 m	809	817

<sup>a</sup> Average values are arithmetic means of band positions for all derivatives studied either in this study or in Ref. [7].

### 2.3. Electropolymerization

A polarographic analyzer PA 2 (Laboratory Devices Prague) with cyclic voltammetric adapter was used for electropolymerization. Polymerization was performed analogously to previously described procedure [3] in a three-electrode cell by repeated cyclic scanning the working electrode potential from  $-0.3$  to  $+1.25$  V at  $50$  mV/s. The Ag/AgCl saturated electrode and Pt plate were used as a reference electrode and an auxiliary one, respectively. The working electrode was a gilded Pt plate (Pt plate diameter  $7.0$  mm, thickness  $0.3$  mm, coated with porous gold layer — thickness of Au layer ca.  $2\text{ }\mu\text{m}$  [3]). Fifteen milligrams of individual 5-nitroquinoxaline species were dissolved in  $5$  ml of glacial acetic acid and then  $0.25$  ml of aqueous  $\text{H}_2\text{SO}_4$  ( $1.0\text{ mol l}^{-1}$ ) was added to increase the conductivity. Firstly, 5-nitroquinoxalines were electrochemically reduced to 5-aminoquinoxalines under the potential  $-1.5$  V (vs. Ag/AgCl) during  $1$  h with exception of a particular experiment with 2,3-dipyrrolyl-5-nitroquinoxaline. Working solutions were purged by nitrogen  $10$  min before polymerization. The formed electrodes were thoroughly washed with distilled water and stored in distilled water.

## 3. Results and discussion

### 3.1. Spectroscopic data of monomer compounds

FT Raman spectra of 5-nitroquinoxalines were mutually compared in the range  $3200$ – $2950$  and  $1650$ – $175\text{ cm}^{-1}$  (Table 1). The range  $3200$ – $2950\text{ cm}^{-1}$  is dominated by characteristic bands of  $\nu(\text{C-H})$  of individual substituents [5,6]. The assignment of some band to  $\nu(\text{C-H})$  of quinoxaline moiety is difficult, because there is no band of analogous intensity in all spectra. Nevertheless, a common band of varying intensity is observed in the range  $3070$ – $3060\text{ cm}^{-1}$ . The specified range is not typical for 5-membered rings, i.e. the band can be attributed to  $\nu(\text{C-H})$  of quinoxaline moiety. All the substituted quinoxalines previously studied [7] exhibit a band in the range  $1625$ – $1600\text{ cm}^{-1}$ ; a weak band at ca.  $1615\text{ cm}^{-1}$  is observed in all measured spectra with exception of the furyl derivative where a band of

analogous intensity and shape is at  $1596\text{ cm}^{-1}$ . A weak band observed at  $1554\text{ cm}^{-1}$  in all spectra with the exception of the furyl derivative ( $1541\text{ cm}^{-1}$ ) could be a ring-stretching mode of the quinoxaline skeleton [7]. The range  $1500$ – $1400\text{ cm}^{-1}$  contains both characteristic bands of ring substituents (Table 1) and some weak common features (e.g. band in the range  $1465$ – $1454\text{ cm}^{-1}$ ) attributed to the quinoxaline skeleton [7]. The most intense common band is located at ca.  $1395\text{ cm}^{-1}$  that is even higher than the interval for previously studied 5-substituted quinoxalines ( $1391$ – $1375\text{ cm}^{-1}$ ) [7]. Many common bands are observed for all compounds close to the average values published for a set of 5-substituted quinoxalines [7] (Table 1). An exception is the band at  $817\text{ cm}^{-1}$  ( $825$ – $813\text{ cm}^{-1}$ ) [7]. We observe a band in ranges  $815$ – $811$  and  $808$ – $804\text{ cm}^{-1}$  for derivatives with 6- and 5-membered rings, respectively. Other well-resolved common bands occur at ca.  $650$  and  $205\text{ cm}^{-1}$ . In addition, characteristic bands of  $\text{NO}_2$  group [5,8] are observed in all the spectra (Table 1). In conclusion, the spectra exhibit both typical features of 5-nitroquinoxaline skeleton and characteristic bands of cyclic substituents confirming the structures proposed (Fig. 1).

### 3.2. Spectroscopic data of electropolymer films

FT SERS spectra of electropolymerized films were compared with each other and with the data of monomers. The only band in the range  $3200$ – $2950\text{ cm}^{-1}$  reliably observed is at  $3063\text{ cm}^{-1}$  in the spectrum of phenyl derivative corresponding to the most intense band of the monomer in this range ( $3064\text{ cm}^{-1}$ ). The spectra of polymers in the range  $1650$ – $1300\text{ cm}^{-1}$  exhibit quite broad bands and differ from the spectra of monomers. Nevertheless, the substituent specific bands can be distinguished with exception of the data of pyrrolyl derivative. The  $1598$ ,  $1497\text{ cm}^{-1}$  bands of the phenyl derivative polymer correspond to the  $1598$ ,  $1498\text{ cm}^{-1}$  of the initial species. Analogously, the  $1589$ ,  $1561$ ,  $1471$ ,  $1433\text{ cm}^{-1}$  bands and  $1592$ ,  $1571$ ,  $1475$ ,  $1442\text{ cm}^{-1}$  bands are the characteristic features of the pyridyl-substituted polymer and monomer, respectively. The  $1524$ ,  $1424$ ,  $1416\text{ cm}^{-1}$  bands of the thienyl substituted polymer correspond to the  $1524$ ,  $1428$ ,  $1418\text{ cm}^{-1}$  bands of the initial species. The two specific bands of furyl group

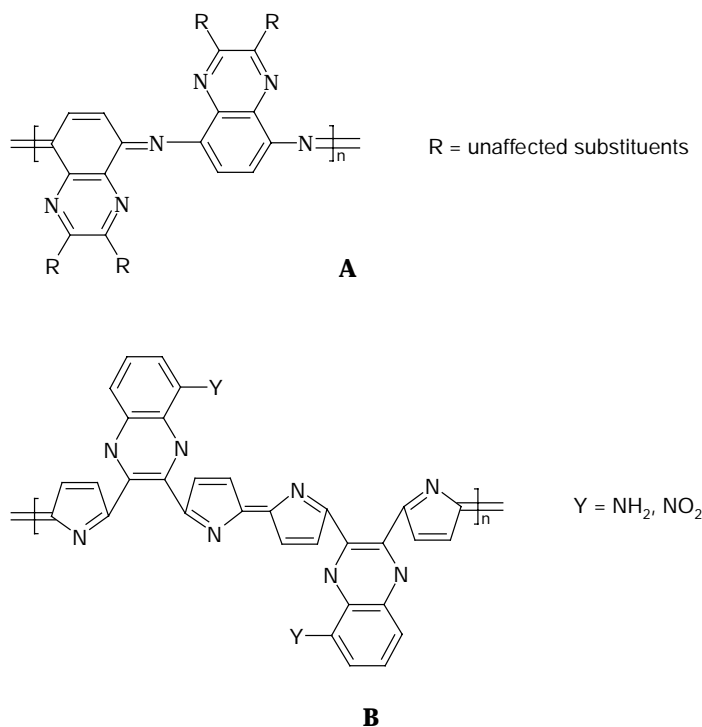


Fig. 2. Proposed structures of electropolymers of 5-aminoquinoxaline derivatives 2,3-disubstituted with (A) 2-furyl, 2-thienyl, phenyl and 2-pyridyl groups and (B) of 2,3-dipyrrol-2'-yl-quinoxaline derivatives.

(1568, 1484  $\text{cm}^{-1}$ ) are not shifted after electropolymerization. No such analogy is observed for the pyrrolyl derivative. New bands at ca. 1562 and 1425  $\text{cm}^{-1}$  are observed in the spectra of all polymers excepting the pyrrolyl derivative. The most intense common band of monomers (1400–1390  $\text{cm}^{-1}$ ) is located in the same range for phenyl, pyridyl and thienyl derivatives. The analogous 1400  $\text{cm}^{-1}$  band in the spectra of furyl monomer and the furyl specific band at ca. 1380  $\text{cm}^{-1}$  are overlapped in the spectrum of polymer film showing a broad band at 1384  $\text{cm}^{-1}$ . The spectrum of pyrrolyl derivative polymer differs completely both from spectra of other polymers and from the spectrum of initial pyrrolyl substituted compound. The most intense band is extremely broad and shifted; two maxima at ca. 1366 and 1355  $\text{cm}^{-1}$  can be resolved. Other weak bands (1494, 1560  $\text{cm}^{-1}$ ) have no counterparts in the spectrum of the monomer (2,3-dipyrrol-2'-yl-5-nitroquinoxaline), but could be compared with the 1488 and 1577  $\text{cm}^{-1}$  bands of a polypyrrole film [9].

Some other corresponding bands of particular

polymer and monomer can be found below 1300  $\text{cm}^{-1}$  excepting the pyrrolyl derivative, e.g. 1031, 1001  $\text{cm}^{-1}$  for the phenyl derivative; 1045, 995  $\text{cm}^{-1}$  for the pyridyl species; 1085, 1055  $\text{cm}^{-1}$  for the thienyl derivative; and 1090, 1020  $\text{cm}^{-1}$  for the furyl species. No such precise analogy is observed for the pyrrolyl derivative. In conclusion, we suggest the electropolymerization does not affect phenyl, 2-pyridyl, 2-thienyl, 2-furyl substituents. Nevertheless the polymerization proceeds, that is indicated by observation of new bands. We propose that the amino groups are primarily involved in polymerization mechanism and that the structure of 5-aminoquinoxaline skeleton is changed via rearrangement of conjugated bonds. The proposed structure of polymer chain (Fig. 2A) is analogous for all derivatives except the 2-pyrrolyl derivative.

The FT Raman data show that the whole skeleton of 2,3-dipyrrol-2'-yl-5-aminoquinoxaline is involved in electropolymerization process. Some analogy with polypyrrole films [9] can be found. The non-reduced 2,3-dipyrrole-2'-yl-5-nitroquinoxaline was electropolymerized to confirm that the pyrrolyl groups are

involved in polymerization. Many similarities of the spectra of the two polymer films show the analogous way of polymerization. The above-mentioned bands (1366, 1494, 1560  $\text{cm}^{-1}$ ) have their counterparts at 1371, 1495, 1561  $\text{cm}^{-1}$  for the non-reduced polymer. Nevertheless, a new band observed at 1518  $\text{cm}^{-1}$  and three bands at 888, 844, 806  $\text{cm}^{-1}$  similar to the initial 5-nitroquinoxaline derivative (886, 852, 808  $\text{cm}^{-1}$ ) indicate the presence of nitro group in the structure of the non-reduced polymer film. To conclude, both 5-amino- and 5-nitro- 2,3-(2'-pyrrolyl)-quinoxalines are primarily polymerized via pyrrolyl groups, but also the system of conjugated bonds of quinoxaline moieties is changed (Fig. 2B). The presence of amino group is not important for polymerization of 2,3-dipyrrol-2'-yl-5-aminoquinoxaline.

### 3.3. Cyclic voltammetry

The cyclic voltammograms are analogous for polymerization of both reduced and non-reduced 2,3-dipyrrole-2'-yl-5-nitroquinoxalines but differ significantly from voltammograms of all other polymerization suggesting different mechanism of electropolymerization of 2,3-dipyrrol-2'-yl-quinoxaline derivatives compared to 2-furyl, 2-thienyl, 2-phenyl and 2-pyridyl substituted quinoxalines. Polymerization of both pyrrolyl derivatives is characterized by an evident peak at ca. 0.7 V (vs. Ag/AgCl sat.), which is growing and shifting to higher potential during reaction. The analogy of this peak indicates that the way of electropolymerization does not depend on the presence of amino group in the monomer. To summarize, an interpretation of cyclic voltammograms agrees with the main result given by Raman spectroscopy of polymer films, i.e. two different types of electropolymerization (Fig. 2). A complete voltammetric and potentiometric study will be published later [4].

## 4. Conclusions

Comparison of FT Raman spectra of 5-nitroqui-

noxaline derivatives shows both evident common features of 5-nitroquinoxaline skeleton and characteristic bands of individual cyclic substituents. The analogy of the type of electropolymerization for 2-furyl, 2-thienyl, 2-pyridyl and phenyl derivatives is demonstrated. These cyclic substituents are not involved in the polymerization. The other type of electropolymerization proceeds for the pyrrolyl derivatives where the structure of whole molecule is changed. This type of polymerization is practically unaffected by the presence of nitro and/or amino group on the quinoxaline skeleton suggesting the primary role of pyrrolyl rings in the polymerization mechanism.

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