

## Electrochromic Properties of 1,3-Di(2-[10-{4-methoxyphenyl}phenothiazin-3-yl]vinyl)benzene

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Electrochemical and spectroelectrochemical properties of molecular glass 1,3-di{2-[10-(4-methoxyphenyl)phenothiazin-3-yl]vinyl}benzene are reported. It exhibits relatively high glass transition temperature (105 °C) and high thermal stability with 5 % weight loss temperature of 352 °C. The amorphous film of the compound showed cathodic and anodic responses with a clear and homogeneous change of color from yellow to violet in the anodic region. At 1.7 V two new absorption bands arise in the Vis absorption spectrum of the compound studied, which are absent at 0 V. One is near 520 nm and the second is at 683 nm. Addition of poly(methylmethacrylate) and poly(N-vinylcaprolactam) enhances electrochromic properties of the material.

*Keywords:* phenothiazine derivative, molecular glass, electrochromic properties, polymers.

### INTRODUCTION

One of the interesting phenomena which is attractive from the point of view of application termed as a “smart” optical device, is electrochromism. It is a reversible electrochemical process accompanied with a color change due to the generation of new electronic absorption transitions in the visible region. Many different classes of organic materials show the electrochromic behavior. A number of low-molar-mass compounds and polymers (e. g., bipyridium salts, polyanilines, polythiophenes) have been described as electrochromic materials [1–5].

Electrochromic devices are used as smart paint and windows, electrochromic rearview mirror in cars, thin flat panel displays [6, 7]. These applications induce the researches connected with the elaboration of new materials with improved electrochromic properties. To be useful for the applications as electrochromic materials organic compounds must demonstrate large changes in transmittance between their oxidized and reduced states, rapid redox switching, long-term stability and good mechanical properties. Taking into account the complex of required properties one of the ways to get such electrochromic materials is elaboration of the molecular mixture of low-molar-mass electrochromic compounds and polymers.

Here we report on the synthesis, electrochemical and spectroelectrochemical studies of one phenothiazine derivative synthesized in our laboratory and on the effect of macromolecules bearing carbonyl groups i. e. polymethylmethacrylate (PMMA) and poly(N-vinylcaprolactam) (PVCa) on its electrochromic behavior. Materials containing phenothiazine moieties are known as fairly good organic semiconductors [8, 9]. However until now, only few studys have been performed on phenothiazine derivatives as electrochromic materials [6].

### EXPERIMENTAL

#### Materials

3-Formyl-10-(p-methoxyphenyl)phenothiazine (1) 1,3-di{2-[10-(4-methoxyphenyl)phenothiazin-3-yl]vinyl}benzene (3) were synthesized as described in our previous works [10, 11]. 1,3-Xylylene-bis(triphenylphosphonium bromide) (2) was synthesized according to the known procedure [12].

#### Measurements

Mass (MS) spectra were obtained on a Waters ZQ (Waters, Milford, USA). Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were obtained using JOEL FX 100 (100 MHz) and Bruker AC 250 (250 MHz) apparatus. Infrared (IR) spectra were recorded using Perkin Elmer Spectrum GX. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on Netzsch instrument STA 409 PC Luxx.

The films for spectroelectrochemical measurements were prepared by the following procedures. Compound 3 was diluted in acetonitrile (concentration was 1 mg/ml). A volume of 0.2 ml of solution was spread onto a ~2 cm<sup>2</sup> ITO coated glass at approximately 1000 rpm for 30 min in airflow (*T* = 45 °C). The observed films were dried at room temperature for 1.5 h. Phenothiazine films were prepared by spraying from 20 mg/ml DMF solution.

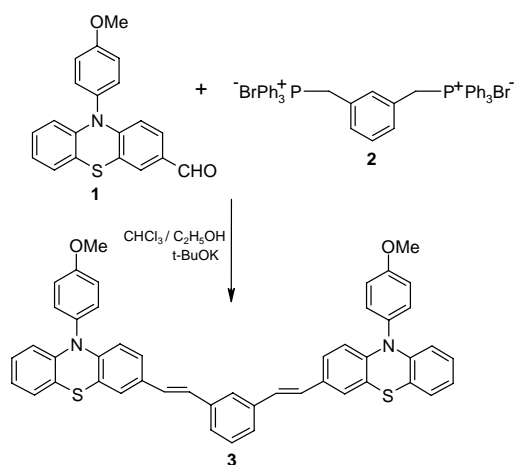
Electrochemical potential control and current sensing were performed using potentiostat/galvanostat Imkor IPC-Pro (Russia). Cyclic voltammetry measurements were performed in three-electrode electrochemical cell in 0.1 M lithium perchlorate solution in acetonitrile as a supporting electrolyte. A platinum electrode was used as a counter electrode and Ag/AgCl electrode was used as a reference electrode.

Spectrophotometric measurements were carried out with Ocean Optics USB2000 spectrophotometer.

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## RESULTS AND DISCUSSION

Compound **3** was obtained as shown in Scheme by Wittig reaction of 3-formyl-10-(p-methoxyphenyl)phenothiazine (**1**) with 1,3-xylylenebis(triphenylphosphonium bromide) (**2**).



### Thermal properties

Compound **3** was isolated after the synthesis as amorphous material. Its DSC curves are given in Fig. 1. The repeated DSC scans revealed only glass transition at 105 °C and no peaks due to crystallization and melting appeared. Compound **3** exhibited relatively high thermal stability. Its 5 % weight loss temperature was observed at 352 °C. Amorphous thin films of compound **3** on substrates could be prepared from its solution by casting or spin coating.

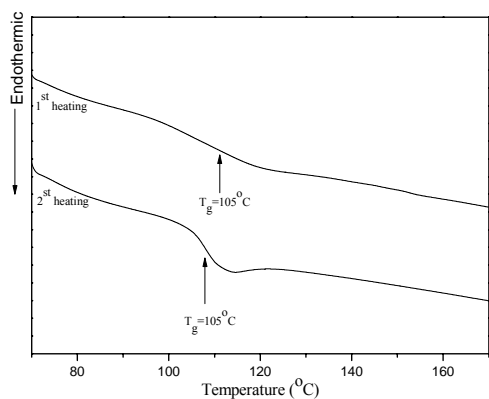


Fig. 1. DSC curve of **3**. Heating rate: 10 °C/min

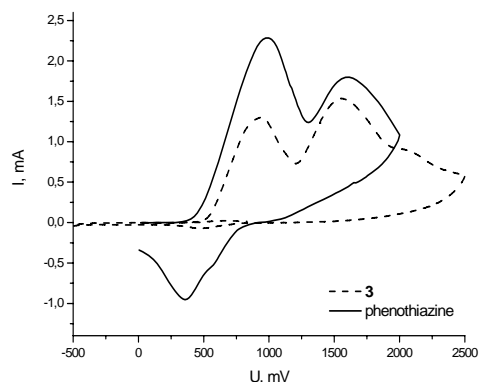
### Electrochemical and spectroelectrochemical properties

Electrochemical oxidation and reduction of compound **3** in spin-coated film was studied by cyclic voltammetry. In order to study the effect of the structure of **3** on its electrochemical activity we compared electrochemical and optical properties compound **3** with those of phenothiazine.

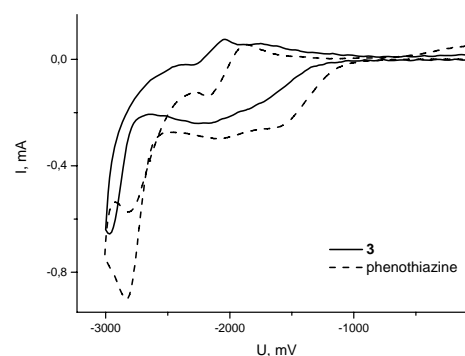
The film of compound **3** showed cathodic and anodic responses with a clear and homogeneous change of color from yellow to violet in the anodic region. Fig. 2, a, shows

a voltammogram of compound **3** and of phenothiazine spin-coated film on ITO glass in 0.1 M LiClO<sub>4</sub> in acetonitrile as a supporting electrolyte in three electrode cell. The oxidation wave, with potential of oxidation of 0.77 V, corresponds to the phenothiazine moiety.

To study the electrochemical and optical properties of **3** and phenothiazine in DMF solutions the two-electrodes cell was used. The tested solution was placed between two ITO glasses with 0.2 mm tetrafluorethylene spacer.



a



b

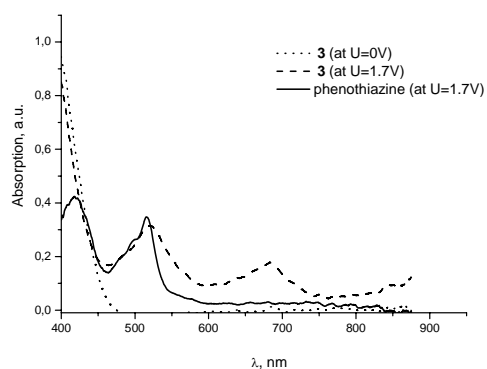
Fig. 2. Cyclic voltammogram: a – of compound **3** and phenothiazine films in (0.1 M LiClO<sub>4</sub>) acetonitrile solution in three electrode cell.; b – of **3** and phenothiazine in DMF solution (concentrations are 5 mM) (0.05 M LiClO<sub>4</sub>) in two electrode cell. Scan rate was 50 mV/s, 1st cycle

The spectroelectrochemical studies of compound **3** and phenothiazine films were performed to analyze the spectral changes induced by redox switching. Fig. 3, a, shows the Vis-absorption spectra of **3** as a function of potential at 0 V and 1.7 V and those of phenothiazine as a function of potential at 1.7 V. At 0 V compound **3** exhibits absorption in the range of 290 nm – 300 nm. No absorption in the visible range is observed. At 1.7 V in the case of **3** two new absorption bands arise. One is near 520 nm and the second is at 683 nm. For phenothiazine under similar conditions only one absorption band at 520 nm is observed. Fig. 3, b, shows absorption spectra of **3** and phenothiazine in DMF solution (concentrations are 5 mM) (0.05 M LiClO<sub>4</sub>) at U = 3 V in two electrode cell.

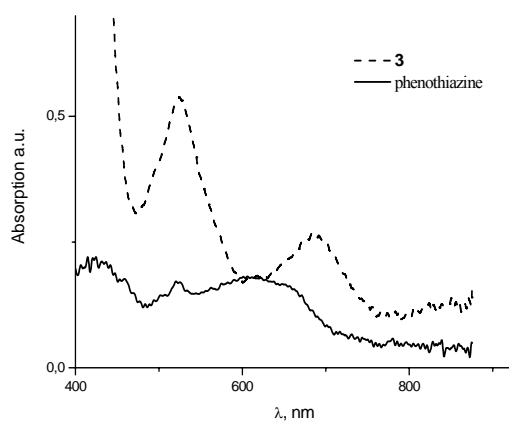
The comparison of extinction coefficients of phenothiazine and compound **3** shows that compound **3** demonstrates higher values of extinction coefficients. Thus extinction coefficient values for phenothiazine are  $\epsilon = 1820$

l/mol·cm at  $\lambda = 620$  nm and  $\epsilon = 1660$  l/mol·cm at  $\lambda = 520$  nm. The values of extinction coefficients for compound **3** are  $\epsilon = 3200$  l/mol·cm at  $\lambda = 680$  nm and  $\epsilon = 5350$  l/mol·cm at  $\lambda = 520$  nm.

We tested the stability of color of **3** polymer film induced by redox switching. The color induced by electrochemical process disappears after 24 hours from the moment of application of the voltage.



a

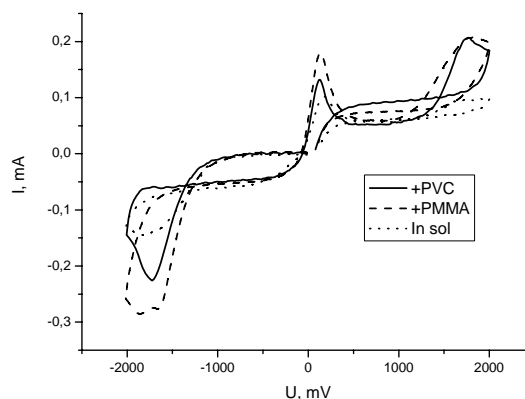


b

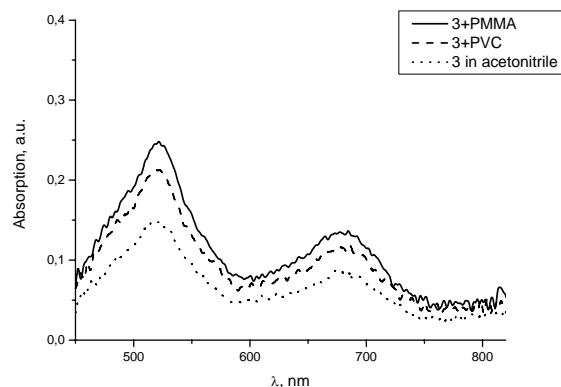
**Fig. 3.** Absorption spectra of **3** and phenothiazine (a) films at  $U = 0$  V or  $U = 1.7$  V in three electrode cell. (b) of **3** and phenothiazine in DMF solutions (concentrations are 5 mM) ( $0.05$  M  $\text{LiClO}_4$ ) at  $U = 3$  V in two electrode cell

In order to study the effect of macromolecules on the electrochemical and optical properties of the synthesized compound macromolecules bearing carbonyl groups i.e. poly(methylmethacrylate) (PMMA) and poly(N-vinylcaprolactam) (PVCa) were used. The polymers were chosen taking into account their complex formation capacity. Cyclic voltammograms of **3** shown in Fig. 4 and absorption spectra shown in Fig. 5 under potential were analyzed in the presence of PMMA and PVCa in two electrode cell in acetonitrile solution. The comparison of current maximum intensity and absorption bands shows that introduction of PMMA as well as PVCa does not effect on the primary behavior of the systems studied. The characteristic wavelengths, corresponding to the absorption maxima of the spectrum and potential of oxidation does not change. However at  $U = 2$  V the maximum of the absorption band and top current are enhanced. The polymers bearing carbonyl groups also influence

electrochromic properties of **3**. The addition of PMMA and PVCa enhances its electrochromic properties. Taking into account the permittivity of acetonitrile ( $\epsilon = 36.2$  l/mol·cm) the observed effect can be explained by the electrostatic interaction between carbonyl groups of macromolecules and **3** which leads to the complex formation.



**Fig. 4.** Cyclic voltammograms of **3** in two electrode cell in acetonitrile solution ( $0.05$  M  $\text{LiClO}_4$ ), PMMA ( $20$  mg/ml) acetonitrile solution ( $0.05$  M  $\text{LiClO}_4$ ), PVCa ( $20$  mg/ml) acetonitrile solution ( $0.05$  M  $\text{LiClO}_4$ ). Scan rate is  $50$  mV/s. 1st cycle. Concentration of **3** is  $1$  mg/ml



**Fig. 5.** Absorption spectra of **3** at  $U = 2$  V in two electrode cell in acetonitrile solution ( $0.05$  M  $\text{LiClO}_4$ ), PMMA ( $20$  mg/ml) acetonitrile solution ( $0.05$  M  $\text{LiClO}_4$ ), PVCa ( $20$  mg/ml) acetonitrile solution ( $0.05$  M  $\text{LiClO}_4$ ). Of **3** concentration is  $1$  mg/ml

## CONCLUSION

We have studied electrochromic properties of phenothiazinylsubstituted ethylene. Glass-forming 1,3-di{2-[10-(4-methoxyphenyl)phenothiazin-3-yl]vinyl}benzene exhibits glass transition temperature of  $105^\circ\text{C}$  and 5% weight loss temperature of  $352^\circ\text{C}$ . The electrochemical studies of the amorphous film of the material revealed cathodic and anodic responses with a clear and homogeneous change of color from yellow to violet in the anodic region. At  $1.7$  V two new absorption bands arise in the absorption spectrum of the compound studied, which are absent at  $0$  V. One is near  $520$  nm and the second is at  $683$  nm. The electrochromic properties of the compound were also analyzed in the presence of polymers. The addition of poly(methylmethacrylate) and poly(N-vinylcaprolactam) enhances its electrochromic properties.

## REFERENCES

1. **Monk, P. M. S.** The Viologens: Synthesis, Physicochemical Properties and Applications of the Salts of 4,4'-Bipyridine. Wiley: Chichester, UK, 1998.
2. **Gao, J., Liu, D.-G., Sansinena, J.-M., Wang, H.-L.** Synthesis and Characterization of Electrochromic Polyamides with Well-defined Molecular Structures and Redox Properties *Advanced Functional Materials* 14 2004: p. 537.
3. **Manisankar, P., Vedhi, C., Selvanathan, G., Somasundaram, R. M.** Electrochemical and Electrochromic Behavior of Novel Poly(aniline-co-4,4'-Diaminodiphenyl Sulfone) *Chemistry of Materials* 17 2005: p. 1722.
4. **Welsh, D. M., Kumar, A., Morvant, M. C., Reynolds, J. R.** Fast Electrochromic Polymers Based on New Poly(3,4-alkylenedioxythiophene) Derivatives *Synthetic Metals* 102 1999: p. 967.
5. **Groenendaal, L., Zotti, G., Aubert, P.-H., Waybright, S. M., Reynolds, J. R.** Electrochemistry of Poly(3,4-alkylenedioxythiophene) Derivatives *Advanced Materials* 15 2003: p. 855.
6. **Argun, A. A., Aubert, P.-H., Thomposon, B. C., Schweideman, I., Gaupp, C. L., Hwang, J., Punto, N. J., Tanner, D. B., MacDiarmid, A. G., Reynolds, J. R.** Multicolored Electrochromism Polymers: Structures and Devices *Chemistry of Materials* 16 2004: p. 4401.
7. **Mortimer, R. J., Dyer, A. L., Reynolds, J. R.** Electrochromic Organic and Polymeric Materials for Display Applications *Displays* 27 2006: p. 2.
8. **Simokaitiene, J., Danilevicius, A., Grigalevicius, S., Grazulevicius, J. V., Getautis, V., Jankauskas, V.** Phenothiazinyl-based Hydrazones as New Hole-transporting Materials for Electrophotographic Photoreceptors *Synthetic Metals* 156 2006: p. 926.
9. **Danilevicius, A., Ostrauskaite, J., Grazulevicius, J. V., Gaidelis, V., Jankauskas, V., Tokarski, Z., Jubran, N., Sidaravicius, J., Grevys, S., Dzena, A.** Photoconductive Glass-forming Phenothiazine-based Hydrazones *Journal of Photochemistry and Photobiology A: Chemistry* 163 2004: p. 523.
10. **Simokaitiene, J., Grigalevicius, S., Grazulevicius, J. V., Rutkaite, R., Kazlauskas, K., Jursenas, S., Jankauskas, V., Sidaravicius, J.** Synthesis, Photophysical and Photoelectrical Properties of Glass-forming Phenothiazinyl- or Carbazolyl-substituted Ethylenes *Journal of Optoelectronics and Advanced Materials* 8 2006: p. 876.
11. **Simokaitiene, J., Laukyte, D., Grazulevicius, J. V., Kazlauskas, K., Jursenas, S., Jankauskas, V.** Phenothiazinyl- and 4-diethylaminophenyl-substituted Diethylenes as Fluorescent and Hole-transporting Molecular Materials *Dyes and Pigments* 81 2009: p. 235.
12. **Wu, T.-Y., Chen, Y.** Poly(phenylene vinylene)-based Copolymers Containing 3,7-phenothiazylene and 2,6-pyridylene Chromophores: Fluorescence Sensors for Acids, Metal Ions, and Oxidation *Journal of Polymer Science Part A: Polymer Chemistry* 42 2004: p. 1272.