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Electrochromic Properties of 4-Ethylenedioxythiophene-2-carbaldehyde N,N-diphenylhydrazone

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Electrochemical and spectroelectrochemical properties of molecular glass 3,4-ethylenedioxythiophene-2-carbaldehyde N,N-diphenylhydrazone are reported. 3,4-ethylenedioxythiophene-2-carbaldehyde N,N-diphenylhydrazone showed glass transition at 37 °C and relatively high thermal stability with the initial decomposition temperature at 219 °C. The amorphous film of the compound showed cathodic and anodic responses with a homogeneous change of color from yellow to blue-green in the anodic region. At 4 V two new absorption bands arise in the absorption spectrum of the compound studied, which are absent at 0 V. One is near 670 nm and the second is at 770 nm. Addition of polymethylmethacrylate and poly(N-vinylcaprolactam) enhances electrochromic properties of the material.

Keywords: electrochromic materials, cyclic voltammetry, 3,4-ethylenedioxythiophene, hydrazone.

1. INTRODUCTION

One of the interesting phenomena, which is attractive with point of view of application as "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. Electrochromic devices are used as smart paint and windows, electrochromic rearview mirror in cars, thin flat panel displays [1, 2]. These applications induce the work related to the elaboration of new materials with electrochromic properties. Different types of organic materials show the electrochromic behavior. 3,4-ethylenedioxythiophene containing compounds are known as anodically active electrochromic materials. Here we report electrochemical and spectroelectrochemical studies of 4-ethylenedioxythiophene-2-carbaldehyde N,N-diphenylhydrazone synthesized in our laboratory. This material and other 4-ethylenedioxythiophene-based hydrazones were earlier reported as fairly effective p-type semiconductors [3, 4].

2. EXPERIMENTAL

2.1. Measurements

Mass (MS) spectra were obtained on a Waters ZQ (Waters, Milford, USA). Proton nuclear magnetic resonance (^{1}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. Thermogravimetric analysis (TGA) was carried out using a METTLER TOLEDO TGA/SDTA 851^e. Differential scanning calorimetry (DSC) was carried out with Perkin–Elmer Diamond DSC.

3,4-Ethylenedioxythiophene-2-carbaldehyde N,N-diphenylhydrazone (**2**) was dissolved in acetonitrile (concentration was 1 mg/ml). A volume of 0.2 ml of solution was spread onto a ~2 cm^2 ITO coated glass at approximately 1000 rpm for 30 min in airflow (T = 45 °C). The obtained films were dried at room temperature for 1.5 h.

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 KCl aqueous solution or 0.1 M lithium perchlorate 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.

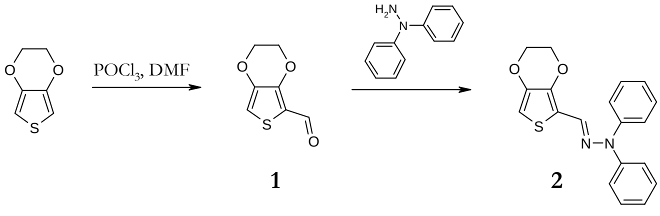
Spectrophotometric measurements were carried out with Ocean Optics USB2000 spectrophotometer.

2.2. Materials

3,4–Ethylenedioxythiophene-2-carbaldehyde (**1**), 3,4-ethylenedioxythiophene-2-carbaldeggbhyde N,N-diphenylhydrazone (**2**) were synthesized as described earlier [3].

3. RESULTS AND DISCUSSION

Hydrazone **2** was synthesized by two-step synthetic route, as shown in Scheme 1. The first step was formylation of 3,4-ethylenedioxythiophene by the Vilsmeier method [5] to get formyl derivative **1** in 76 % yield. The second step was condensation of aldehyde **1** with N,N-diphenylhydrazine hydrochloride to obtain the target compound **2**.



Scheme 1. Synthetic route to compounds **1**, **2**

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The glass forming ability of compound **2** was studied by DSC. The first DSC scan of the sample of hydrazone **2** revealed endothermic melting signal at 172 °C, but after slow cooling the second heating scan revealed only glass transition at 37 °C. Amorphous thin films of compound **2** on substrates can be prepared from its solution by casting or spin coating. The thermal stability of compound **2** is similar to that of earlier reported aromatic hydrazones [6, 7]. The temperature of the onset of thermal degradation of **2** in the atmosphere of inert gasses is 219 °C.

Electrochemical oxidation and reduction of 3,4-ethylenedioxythiophene-2-carbaldehyde N,N-diphenylhydrazone (**2**) in spin-coated film was studied by cyclic voltammetry. The film showed cathodic and anodic responses with a even change of color from yellow to blue-green in the anodic region. Figure 1 shows a voltammogram of spin-coated film of **2** over ITO glass in 0.1 M KCl in water as a supporting electrolyte in three electrode cell. The oxidation wave, with oxidation potential at 1.28 V, is clearly seen in Figure 1.

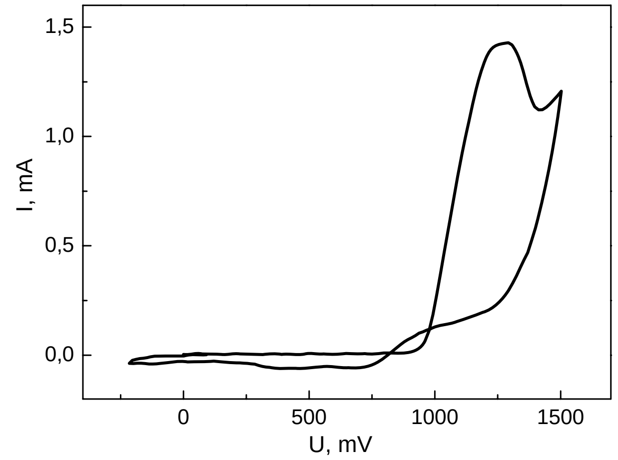

Fig. 1. Cyclic voltammogram of spin-coated film of **2** in 0.1 M KCl aqueous solution as a supporting electrolyte in three electrode cell. Scan rate: 50 mV/s. 1st cycle

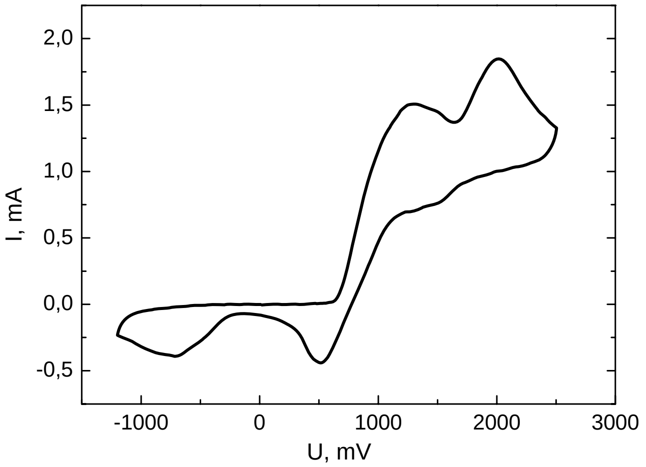

Fig. 2. Cyclic voltammogram of **2** in 0.1 M $LiClO_4$ acetonitrile solution in three electrode cell. Concentration of **2** is 1 mg/ml. Scan rate: 50 mV/s. 1st cycle. Working electrode – ITO coated glass

Figure 2 demonstrates cyclic voltammogram of **2** in 0.1 M $LiClO_4$ acetonitrile solution in three electrode cell. The oxidation wave, with oxidation potential of 1.29 V is observed. Thus low-molar-mass electrolyte (KCl / $LiClO_4$) does not influence the electrochemical parameters of 3,4-ethylenedioxythiophene-2-carbaldehyde N,N-diphenylhydrazone (**2**). After the first cycle compound **2** remains colored both in film and in solution.

The spectroelectrochemical measurements of the film of compound **2** were performed in order to analyze the spectral changes induced by redox switching. Figure 3 shows the absorption spectra of spin-coated film of **2** at $U = 4$ V (1) and at $U = 0$ V (2) (in aqueous solution). At 0 V compound **2** exhibits absorption in the UV region. No absorption in the visible range is observed. At 2 V two absorption bands arise. One is near 670 nm and the second is at 770 nm.

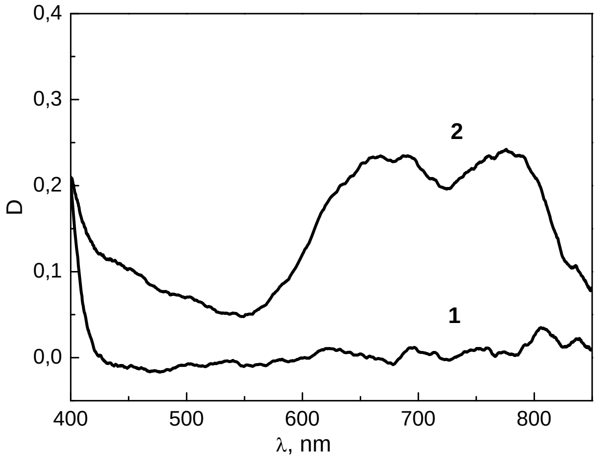

Fig. 3. Absorption spectra of spin-coated film of **2** at $U = 0$ V (1) and 1.4 V (2) (in aqueous solution)

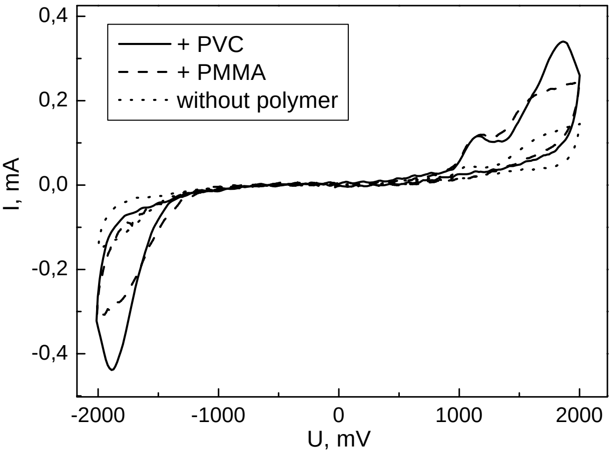

Fig. 4. Cyclic voltammograms of **2** in two electrode cell in acetonitrile solution (0.05 M $LiClO_4$), PMMA (20 mg/ml) acetonitrile solution (0.05 M $LiClO_4$), PVCa (20 mg/ml) acetonitrile solution (0.05 M $LiClO_4$). Scan rate: 50 mV/s. 1st cycle. The concentration of **2** is 1 mg/ml

The effect of polymer on the electrochromic properties of 3,4-ethylenedioxythiophene-2-carbaldehyde N,N-diphenylhydrazone (**2**) was studied. The two-electrodes cell was used for the investigation of electrochromic properties of **2** in solutions in the presence of polymers. The tested solutions were placed between two ITO glasses with 0.2 mm tetrafluorethylene spacer. The cyclic voltammograms (Fig. 4) and absorption spectra (Fig. 5) of **2** were recorded at $U = 2$ V in the presence of polymethylmethacrylate (PMMA) and poly(N-vinylcaprolactam) (PVCa) in two electrode cell in acetonitrile solution. For the comparison the cyclic voltammogram and absorption spectrum obtained in the absence of polymers are shown in Fig. 4 and Fig. 5, respectively.

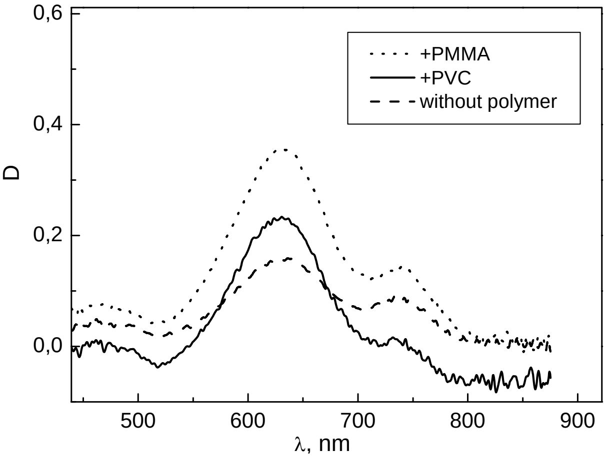

Fig. 5. Absorption spectra of **2** at $U = 2$ V in two electrode cell in acetonitrile solution (0.05 M $LiClO_4$), PMMA (20 mg/ml) acetonitrile solution (0.05 M $LiClO_4$), PVCa (20 mg/ml) acetonitrile solution (0.05 M $LiClO_4$). The concentration of **2** is 1 mg/ml

The molar extinction coefficients of **2** at $\lambda = 630$ nm in the presence of polymer and without it are shown in Table 1.

Table 1. Molar extinction coefficients of **2** at $\lambda = 630$ nm

Sample	ε_{630} l/mole·cm
2	2837
2 + PMMA	6529
2 + PVCa	5590

The obtained results show that the addition of PMMA and PVCa leads to the increase of extinction coefficients in the of 3,4-ethylenedioxythiophene-2-carbaldehyde N,N-diphenylhydrazone (**2**) at $\lambda = 630$ nm. This effect is more significant in the case of PMMA. However, at $\lambda = 735$ nm the extinction coefficient of 3,4-ethylenedioxythiophene-2-carbaldehyde N,N-diphenylhydrazone is only slightly influenced by the addition of both PMMA and PVCa.

4. CONCLUSIONS

In conclusion we have studied electrochromic properties of 3,4-ethylenedioxythiophene-2-carbaldehyde N,N-diphenylhydrazone. Glass-forming 3,4-ethylenedioxythiophene-2-carbaldehyde N,N-diphenylhydrazone exhibits glass transition temperature of 37 °C and initial decomposition temperature of 352 °C. The electrochemical studies of the amorphous film of the material revealed cathodic and anodic responses with a even change of color from yellow to blue-green in the anodic region. At 4 V two new absorption bands arise in the absorption spectrum of the compound studied, which are absent at 0 V. One is near 670 nm and the second is at 770 nm. Addition of polymethylmethacrylate and poly(N-vinylcaprolactam) enhances electrochromic properties of the material.

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