



Dipyrromethane functionalized monomers as precursors of electrochromic polymers

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ABSTRACT

Dipyrromethane functionalized monomers **1–4** have been synthesized and characterized using spectroscopic methods and X-ray diffraction analysis (monomer **4** and dialdehydes **5** and **6**). Monomers exhibit irreversible electrochemical oxidation but during multiple oxidation cycles electropolymerization of monomers on the electrode surface occurs. Electrochemical polymerization of monomers were carried out in acetonitrile solution using tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte. It was found that faster electropolymerization occurs when monomer contains more than one dipyrromethane unit and obtained polymers have better stability. The morphology of polymer films on ITO electrodes was analyzed by SEM and AFM techniques. It was found that polymers obtained by electropolymerization method are homogenous and uniform with low roughness, RMS value: 105 Å and 153 Å for **poly-1** and **poly-2** respectively. Obtained thin films of polymers **poly-1** and **poly-2** exhibit interesting optical properties dependent on the core of monomer and were used as active layers for the construction of electrochromic devices. The colors of oxidized states of electrochromic polymers can be easily modified by the change of electroactive cores in monomers.

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1. Introduction

Electrochromic materials have received a great attention in recent years due to their applications as active layers in a wide range of device types, such as e-papers [1], smart windows and mirrors [2–4], and dynamic camouflage technologies [5,6]. Electrochromism is defined as the capability of the material to changes of its optical properties in response to an external electric stimulus. Many classes of inorganic [7–9] and organic [10–12] compounds have been examined as electrochromic materials, but conjugated polymers due to the wide range of colors in both neutral and charged states spreading from the UV region through visible to the NIR are the most promising compounds for plastic electronics [13,14]. Conjugated polymers can be printed on different substrates what makes the possibility of fabrication of many types of flexible devices [15–18].

One of the ways to obtain a stable thin film is electropolymerization, which only requires a good solubility of monomers and the polymeric film is *in situ* deposited on the electrode surface

[19]. With appropriate electropolymerizable groups, such as thiophene, pyrrole, triphenylamine and vinyl groups, both oxidative and reductive electropolymerization is possible [20–23]. Obtained in this way thin films have good adhesion and electrical contact to the electrode surface. Among the numerous conducting polymers, polypyrrole are one of the most interesting materials for coating of fabrics [24], electromagnetic shielding [25], construction of sensors [26], batteries [27] and supercapacitors [28]. Many different mechanisms of electropolymerization of pyrrole depending on electrolyte, solvent, temperature and pH are known [29].

Dipyrromethanes are important building blocks for the synthesis of a variety of functional porphyrins [30], porphyrinoids [31], calixpyrroles [32] and BODIPY dyes [33]. Meso-substituted dipyrromethanes can be easily prepared in the direct condensation reaction of carbonyl compounds with excess of pyrrole in the presence of acid catalysts such as propionic acid, trifluoroacetic acid (TFA) or BF₃·etherate. Many of bispyrro-substituted compounds have been prepared to investigate anion-binding properties [34–37]. Dipyrromethanes are known to undergo oxidative electrochemical polymerization. This protocol was successfully used for the preparation of thin films of polymers on the electrode surface [38–40] for the construction of electrochromic devices with a good optical contrast, switch time and stability [39].

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In this paper we report a series of dipyrromethane functionalized monomers **1–4** (Fig. 1), their electrochemical polymerization on the electrode surface, electrochromic properties of obtained polymers and their use as active materials in construction of the transmission window type electrochromic devices. Synthesis and anion-binding properties of monomer **4** has been previously reported [34] but no electrochemical properties were discussed.

2. Experimental section

2.1. General information

Reagents were used without further purification as supplied from Aldrich or Fluorochem. NMR spectra were run on a Bruker Ultra 300 MHz spectrometer and were calibrated against the residual protonated solvent signals (CDCl_3 , δ 7.24, CD_3CN δ 1.94 ppm) and shifts are given in parts per million. ESI mass spectra for acetonitrile solutions $\sim 10^{-4}$ M were measured using a Waters Micromass ZQ spectrometer. Microanalyses were obtained using a Vario EL III CHN element analyzer. SEM images were done on the scanning electron microscope Quanta 250 FEG, FEI. AFM measurements were done on the Agilent 5500.

2.2. Electrochemical

Electrochemical measurements were performed on a multi-channel BioLogic VSP potentiostat. Compounds were dissolved in anhydrous and deaerated acetonitrile at 10^{-4} M with 0.1 M tetrabutylammonium hexafluorophosphate as the electrolyte. A platinum electrode was used as the working electrode with a platinum wire as the auxiliary electrode and the silver wire as a pseudoreference electrode. All electrochemical measurements were done at 100 mV/s scan rate at room temperature. To obtain the oxidation potentials (E_{pa}) or $E_{1/2}$ of monomers and polymers, ferrocene assumption [41] was used. In this method ferrocene was used as an internal standard and the voltammograms were calibrated against its reversible ferrocene-ferrocenium (Fc/Fc^+) redox couple ($E^{\circ} = 0.40$ V vs. SCE) in CH_3CN with 0.1 M TBAPF₆ as electrolyte [42]. To obtain oxidation potentials of monomers ferrocene was added to the solution of monomer and cyclic voltammogram was recorded. In case of polymers, first the electropolymerization of monomers on Pt working electrode was performed, electrode was

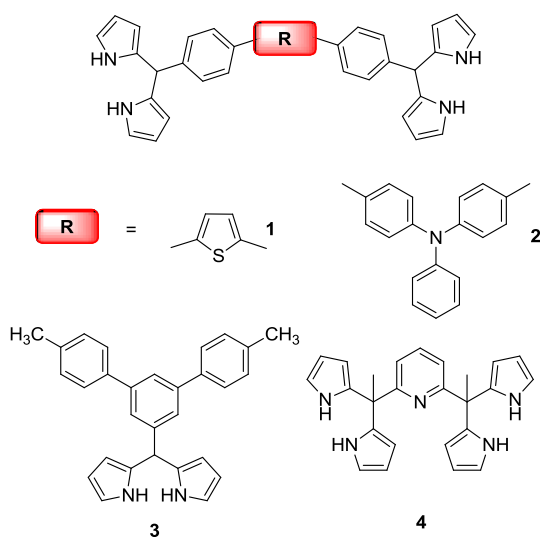


Fig. 1. Structures of monomers **1–4**.

rinsed with acetonitrile to remove unreacted monomers and cyclic voltammogram of polymer was recorded in a monomer-free solution containing ferrocene as internal standard.

Spectroelectrochemical measurements were done using a multi-channel BioLogic VSP potentiostat connected to a Jasco V-770 UV–vis–NIR spectrometer. ITO plates were used as the working electrode with a platinum wire as the auxiliary electrode and the silver wire as a pseudoreference electrode. Before polymerization, ITO plates were cleaned by the sonication in water for 15 min, followed by the sonication in 2-propanol for 15 min, dried and cleaned by ozone generation using the Ossila UV-ozone cleaner.

2.3. Preparation of gel electrolyte

The gel electrolyte was prepared by using LiClO_4 :acetonitrile:PMMA (average $M_w \sim 120,000$ by GPC, Aldrich):PC in the weight ratio of 3:70:7:20. When LiClO_4 was dissolved in acetonitrile, PMMA was added into the solution and mixture was vigorously stirred and heated until all PMMA was dissolved. Propylene carbonate was added and the reaction mixture was stirred and heated until the highly conducting transparent gel was obtained.

2.4. Construction of electrochromic devices

Transmissive window-type electrochromic devices were fabricated using ITO coated glass as the working electrodes. A frame of double-sided adhesive tape was placed on the conductive side of a pristine 2 cm \times 2 cm ITO-coated glass slide. The gel electrolyte was then spread inside the frame with a spatula. A second ITO-glass slide coated with a layer of the immobilized **poly-1** or **poly-2** was placed face-down on the gel coated slide. The two electrodes were then pressed together. Copper tape was applied to the bare ITO on both slides of the device as electrical contacts.

2.5. X-ray crystallography

Diffraction data were collected by the ω -scan technique, for **4** at room temperature, for **5** at 110 (1) K, and for **6** at 130 (1) K, on Rigaku Xcalibur four-circle diffractometer with Eos CCD detector and graphite-monochromated MoK_α radiation ($\lambda = 0.71069$ Å). The data were corrected for Lorentz-polarization as well as for absorption effects [43]. Precise unit-cell parameters were determined by a least-squares fit of 2627 (**4**), 1035 (**5**), and 6656 (**6**) reflections of the highest intensity, chosen from the whole experiment. The structures were solved with SHELXT [44] and refined with the full-matrix least-squares procedure on F^2 by SHELXL-2013 [44]. All non-hydrogen atoms were refined anisotropically, hydrogen atoms in **6** and **5** were placed in idealized positions and refined as 'riding model' with isotropic displacement parameters set at 1.2 times U_{eq} of appropriate carrier atoms, in **4** hydrogen atoms were found in the difference Fourier map and isotropically refined.

Crystal data:

4: $\text{C}_{25}\text{H}_{25}\text{N}_5$, $M_r = 395.50$, monoclinic, $P2_1/n$, $a = 12.3456$ (10) Å, $b = 13.7801$ (11) Å, $c = 12.4906$ (8) Å, $\beta = 91.981$ (7)°, $V = 2123.7$ (3) Å³, $Z = 4$, $d_x = 1.24$ g cm⁻³, $\mu = 0.076$ mm⁻¹, $F(000) = 840$. 14904 reflections collected up to $2\theta = 27.0^\circ$, 4292 symmetry independent ($R_{\text{int}} = 3.27\%$), 3058 with $I > 2\sigma(I)$. Final R [$I > 2\sigma(I)$] = 4.74%, $wR2$ [$I > 2\sigma(I)$] = 9.69%, R [all refl.] = 7.69%, $wR2$ [all refl.] = 11.08%, $S = 1.07$, max/min $\Delta\rho = 0.17/-0.16$ e. Å⁻³.
5: $\text{C}_{18}\text{H}_{12}\text{O}_2\text{S}$, $M_r = 292.34$, monoclinic, $P2_1$, $a = 9.6758$ (6) Å, $b = 5.8738$ (4) Å, $c = 11.9198$ (11) Å, $\beta = 91.847$ (7)°, $V = 677.09$ (9) Å³, $Z = 2$, $d_x = 1.43$ g cm⁻³, $\mu = 0.240$ mm⁻¹, $F(000) = 304$. 2399 reflections collected up to $2\theta = 26.5^\circ$, 1835 symmetry independent ($R_{\text{int}} = 1.80\%$), 1736 with $I > 2\sigma(I)$. Final R

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