



A magenta polypyrrole derivatised with Methyl Red azo dye: synthesis and spectroelectrochemical characterisation



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ABSTRACT

A pyrrole derivative bearing 2-(4-dimethylaminophenylazo)benzoic acid, also known as Methyl Red (MR), was prepared by a simple synthetic route, and electropolymerised onto ITO/glass electrodes in $(C_4H_9)_4NBF_4/CH_3CN$ in presence of boron trifluoride diethyl etherate (BFEE). Films of polypyrrole (PPy) and PPy doped with MR (PPy/MR) were also deposited onto ITO/glass in order to compare their electrochromic properties with the films of PPy derivatised with MR. Cyclic voltammogram of the poly[3-(N-pyrrolyl)propyl 2-(4-dimethylaminophenylazo)benzoate] (PMRPy) film displayed a redox pair with anodic peak potential (E_{pa}) at ca. 0.53 V and cathodic peak potential (E_{pc}) at 0.25 V vs. Ag/Ag^+ , corresponding to the polymer *p*-doping, whilst the PPy/MR film shows capacitive behaviour with a redox pair in the cathodic region ($E_{pa} = -0.36$ V and $E_{pc} = -0.62$ V), similar to the PPy film ($E_{pa} = -0.10$ V, and $E_{pc} = -0.15$ V), and an anodic wave in the same potential range of that for PMRPy film. The electrochromic properties of the PMRPy film, such as chromatic contrast ($\Delta\%T = 34.2\%$), switching time ($\tau = 10$ s) and stability ($\Delta\%T = 15\%$ at the 100th cycle), were enhanced relative to the PPy/MR and PPy films. However, the colour of the PMRPy film changed from yellow (-0.8 V) to magenta ($E = 1.0$ V) in the first cycle and became light magenta at -0.8 V in the subsequent cycles. PMRPy films were also investigated in phosphate buffer solution (PBS, $2.0 \leq pH \leq 9.0$) and after exposure to HCl vapour, in which the colour varied from magenta at $pH = 2.0$ to yellow at $pH = 9.0$. Such properties are interesting for application in pH sensors.

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1. Introduction

One of the major challenges in the area of molecular electronics is focused toward the synthesis of materials based on conjugated polymers with novel optoelectronic properties, such as electrochromism, electrochromism, third-order non-linear optics and chemical sensing [1,2]. Therefore, designing of hybrid systems based on oligomers and π -conjugated polymers having variable optical properties, striking chromic effects, enhanced performance, and narrow band gap energy remains important [3].

Organic dyes have been used in different areas of science, such as medicine, physics, and chemistry, to produce chromatic changes or to investigate the effect of a light absorber specimen in well-

known systems. Therefore, the enhancement of optical contrast and colour modulation of π -conjugated polymers and their hybrid materials can be easily achieved by incorporating organic dyes (such as Indigo Carmine [4], Bromophenol Blue [5], Brilliant Yellow [6], Ponceau 4R [7], Remazol Black B and Dianix Red [8]) to the polymer film, or even by the modification of the monomer/polymer structure by derivatisation with a dye. Using this approach, Cihaner and Algi [9] prepared a copolymer of a 2,5-di(2-thienyl)pyrrole (SNS) derivatised with an azo dye and 3,4-ethylenedioxythiophene (EDOT), and Ajayaghosh et al. [3] synthesised soluble donor-acceptor type conjugated copolymers of N-alkylpyrroles and squaric acid, in order to achieve better optoelectronic properties in comparison with the non-modified polymers.

Among π -conjugated polymers, polypyrrole (PPy) and its derivatives are particularly important due to their good electric conductivity and chemical stability in ambient atmosphere, besides their structural versatility, which allows tailoring of their

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electronic and electrochemical properties by the manipulation of the monomer structure [10–12]. The incorporation of azo-aromatic dyes, such as Methyl Red (2-[4-(dimethylamino)phenylazo]benzoic acid), into the polymer backbone would be quite interesting due to their reversible optoelectronic properties [9,13–16]. Methyl Red (MR) is a well-known pH indicator having dimethylamine-, azo- and carbonyl- groups in its chemical structure [17], which is promising to modify and/or interact with different materials.

As MR presents different colours associated to pH variations, such as red (acid medium), orange and yellow (basic medium), we take advantage of this characteristic in order to obtain electroactive polymer films based on a pyrrole (Py) derivatised with MR deposited onto ITO/glass electrodes, in which the colour of the films varied from magenta (acid medium) to yellow (basic medium) according to the pH. In spite of the large number of recent papers and reviews describing the synthesis, spectroelectrochemical properties and applications of PPy derivatives, there are, to our knowledge, only a few reports concerning the preparation and properties of magenta films of PPy derivatives and/or their copolymers [9,11,12,18].

Electroactive polymer films that present magenta colour are important for development of non-emissive display technologies, since these electrochromic displays are assembled using materials that can exhibit three primary colours and can be employed to create full colour displays where the expression of any colour can be achieved through the control of the intensity of each of the primary colours [19,20].

Colour mixing in display technologies works using the principle of colour as a light and involves mixing RGB (red, green, blue) colours in varying intensities to create a multitude of colours. Similarly, subtractive primary colours CMY (cyan, yellow, magenta) can also be mixed to produce new colours. Mixing these three colours produces black, absence of light, which is also included in the colour mixing systems, and usually subtractive primary colours are represented as CMYK where “K” stands for “black” [21]. Therefore, when cyan and magenta mix, or overlap, they create blue; when yellow and magenta mix, they create red; when cyan and yellow mix, they create green; and finally, when cyan, magenta, and yellow mix, they create black [22]. So, it is possible successfully obtain multiple colours including intermediate red, green, and blue colours according to a subtractive colour-mixture process.

On the basis of this approach, we expect that the magenta polymer based on Py derivatised with MR, so-called PMRPy, be useful as active layer in assemble of multicoloured optoelectronic devices based on CMYK system, as well as in pH sensors.

Furthermore, in order to investigate the electrochromic properties of PPy films modified with a dye according to the preparation method, we also electrodeposited films of PPy doped with MR.

2. Experimental

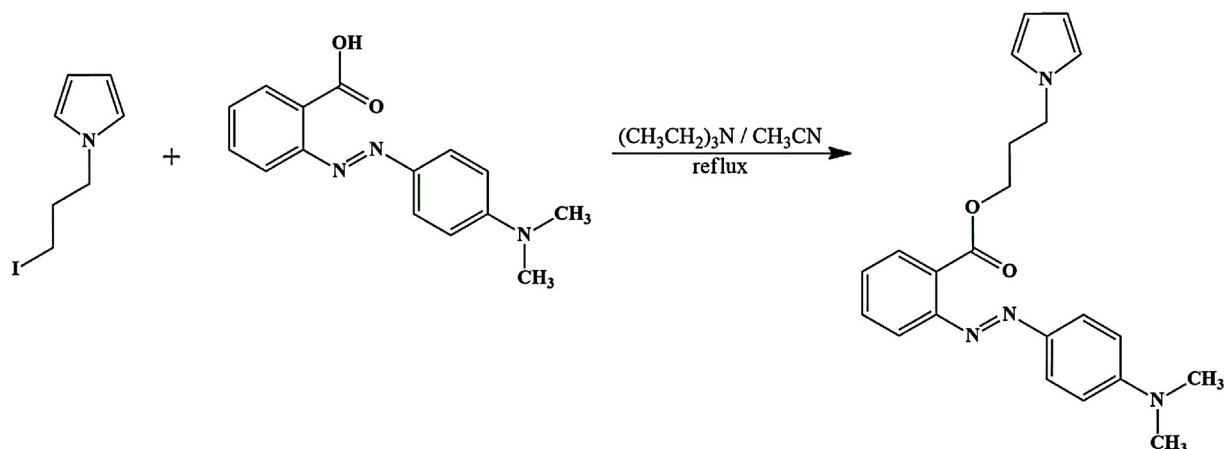
2.1. Materials and instrumentation

All the chemical reagents for synthesis were purchased from Sigma-Aldrich or Acros and used as received. Anhydrous acetonitrile 99.8% (CH_3CN <0.001% water, Sigma-Aldrich), tetrabutylammonium tetrafluoroborate ($(\text{C}_4\text{H}_9)_4\text{NBF}_4$, Aldrich), lithium perchlorate (LiClO_4 , Aldrich) and sodium dodecylsulphate (SDS, Sigma) were used as received, boron trifluoride diethyl etherate (BFEE, Sigma-Aldrich) was freshly distilled before use. Phosphate buffer solutions (PBS) were prepared with pH varying from 2.0 to 9.0.

NMR spectra were recorded on a Bruker spectrometer operating at a frequency of 400 MHz. The FTIR spectrum was acquired on a Bruker IFS66 spectrophotometer. A Hewlett-Packard 8453 diode array spectrophotometer was used for the ultraviolet-visible-near infrared (UV-vis-NIR) spectra acquisition in the spectroelectrochemical experiments.

2.2. Synthesis of 3-(*N*-pyrrolyl)propyl 2-(4-dimethylaminophenylazo) benzoate (MRPy)

1-(3-Iodopropyl)pyrrole (0.50 g, 2.10 mmol), methyl red (0.56 g, 2.10 mmol) and triethylamine (0.58 mL, 4.20 mmol) were added to dry CH_3CN (20 mL). The reaction mixture was stirred at 80 °C for 3 h. After this period, the reaction mixture was extracted with 30 mL of $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ (1:1, v/v) and the organic phase was evaporated in a rotatory evaporator. The crude product was purified by chromatography on silica gel (230–400 Mesh) using CH_2Cl_2 as eluent, to give 0.454 g (57% yield) of the MRPy as a red viscous liquid, **Scheme 1**. ^1H NMR (400 MHz, CDCl_3), δ (ppm): 7.89 (dt, 2H), 7.79 (dd, 1H), 7.61 (m, 1H), 7.42 (m, 1H), 6.78 (d, 2H), 6.55 (t, 2H), 6.12 (t, 2H), 4.32 (t, 2H), 3.89 (t, 2H), 3.11 (s, 6H), 2.11 (m, 2H). ^{13}C NMR (400 MHz, CDCl_3), δ (ppm): 168.25, 152.75, 152.65, 131.78, 129.66, 128.31, 127.89, 125.42, 120.54, 119.40, 111.58, 108.16, 62.40, 46.12, 40.422, 30.65. FTIR (ATR): 3099 (w, ν (C-H $_{\alpha}$ pyrrole)), 2920 (m, ν_{as} (C-H)), 2808 (m, ν_{as} (C-H)), 1724 (s, ν (C=O)), 1597 (m, ν_{as} (C=C)), 1364 (s, δ (N-C)), 1244 (m, δ (C-H)), 1141 (s, ν (C-O)), 750 (s, $\delta_{\text{out-of-plane}}$ (C-H substituted benzene)), 723 (s, $\delta_{\text{out-of-plane}}$ (C-H $_{\alpha}$ pyrrole)) cm^{-1} .



Scheme 1. Synthetic route to obtain MRPy.

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