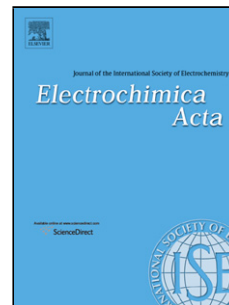


Accepted Manuscript

Title: Multielectrochromism of redox states of thin electropolymerised films of poly(3-dodecylpyrrole) involving a black coloured state

Author: Tomasz Jarosz Alina Brzeczek Krzysztof Walczak
Mieczyslaw Lapkowski Wojciech Domagala



PII: S0013-4686(14)01200-6
DOI: <http://dx.doi.org/doi:10.1016/j.electacta.2014.06.018>
Reference: EA 22880

To appear in: *Electrochimica Acta*

Received date: 9-3-2014
Revised date: 3-5-2014
Accepted date: 3-6-2014

Please cite this article as: T. Jarosz, A. Brzeczek, K. Walczak, M. Lapkowski, W. Domagala, Multielectrochromism of redox states of thin electropolymerised films of poly(3-dodecylpyrrole) involving a black coloured state, *Electrochimica Acta* (2014), <http://dx.doi.org/10.1016/j.electacta.2014.06.018>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Multielectrochromism of redox states of thin electropolymerised films of poly(3-dodecylpyrrole) involving a black coloured state

Tomasz Jarosz^a, Alina Brzeczek^a, Krzysztof Walczak^a, Mieczysław Lapkowski^{a,b,1}, Wojciech Domagala^{a,*}

^aFaculty of Chemistry, Silesian University of Technology, Marcina Strzody 9 street, 44-100 Gliwice, Poland

^bCenter of Polymer and Carbon Materials, Polish Academy of Science, 41-819 Zabrze, Poland

*Corresponding Author, wojciech.domagala@polsl.pl tel. +48 32 237 1305, Postal address: 9 Marcina Strzody street, 44-100 Gliwice POLAND
¹ISE member

Keywords: pyrrole; alkylpyrrole; EPR UV-Vis-NIR spectroelectrochemistry; electrochromism; transmissive to black

Abstract:

Thin films of poly(3-dodecylpyrrole) have been found to yield multi-electrochromic characteristics. Optimisation of the polymer electrodeposition process enabled fabrication of layers exhibiting three distinct colourations at different oxidation levels. Coupled EPR-UV-Vis-NIR spectroelectrochemistry enabled correlation of these colour changes with the formation and decay of polaron and bipolaron charge carriers, offering an insight into the mechanism of doping / dedoping processes taking place in this polymer. The ionisation potential of the polymer was found to be very low, with valence band edge located at -3.7 eV, explaining the relative oxidation ease of the polymer and accounting for an ample number of spins present in the electrochemically dedoped polymer film. Maximum optical contrast of up to 15% and a visible light range averaged one of 10% was observed. Dynamic colour switching contrast of 10% is attainable at 5 s switching time, while switching steps as short as 0.5 s afford 6% contrast value. The fully oxidised polymer features broad UV-Vis absorption, making the system an interesting candidate for transmissive-to-black electrochromic devices.

1. Introduction

In recent years, the pursuit of transparent-to-black electrochromic materials has become preeminent among various research trends in applied electrochromism. Intensive research is being carried out in this area and a number of systems exhibiting bright-to-dark electrochromism have been reported to date [1,2,3,4,5]. Several approaches to obtaining the desired chromatic effect are distinguishable among existing reports. These have been progressively evolving from multi-layered arrangements of electrochromic materials, through single-layered copolymer devices and, ultimately, to single layer homopolymer systems. We add our contribution to this

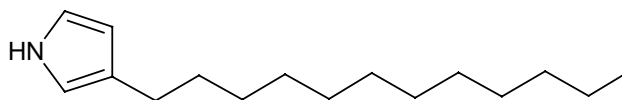
exciting research field by presenting a simple alkylpyrrole polymer, combining two advantageous qualities of an electrochromic material: multi-electrochromism and black colouration.

Investigation of poly(3-alkylpyrroles) has been the subject of works by multiple groups [6,7,8,9,10,11,12,13,14]. These studies focused on several material properties, however, only a narrow spectroelectrochemical survey was carried out. Electrochromism was observed only qualitatively, therefore, numerical values characterising it were not reported. Poly(3-methylpyrrole) and poly(3-octylpyrrole) were shown to exhibit electrochromic properties, and their relatively featureless visible range spectra hinted at the possibility of developing a black absorptive state similar to the one observed by Diaz et al. for electrosynthesised unsubstituted polypyrrole [15]. Interestingly, no pursuit was made to explore this tentative possibility. Longer alkyl chain derivatives have been prepared both electrochemically [16] and chemically [17] and studied, howbeit, primarily with the goal of elucidating the doping mechanism of this class of polymers [Error! Bookmark not defined.,18]. Furthermore, the good solubility of these systems has been well exploited, as evidenced by their application as coatings for textiles [19,20].

Revisiting this field, we have found that 3-dodecylpyrrole (3DDP) yields polymers featuring surprising chromic qualities. Firstly, poly(3DDP) films exhibit three distinct colourations, a rare quality for simple homopolymer systems. Secondly, one of its oxidised states is found to display black colouration, supplementing a scarce group of π -conjugated homopolymers manifesting this sterling trait. Thirdly, reasonable visible range averaged optical contrast is registered for the switch between the oxidised and reduced forms of this polymer. Considering practical aspects, 3-dodecylpyrrole can be synthesised in a simple, classic reaction sequence, adding further merit to this electrochromic system.

2. Experimental

3-dodecylpyrrole (**3DDP**) has been synthesised, using a modification of the method reported by Wallace et al. [Error! Bookmark not defined.]. Details of the employed synthetic protocol can be found in the Supplementary Information.



3DDP

Electrochemical investigations were performed using a standard three-electrode cell, with platinum wire or indium-tin oxide (ITO) coated quartz slides (Precision Glass & Optics, $20 \pm 5 \Omega/\text{sq}$, $9 \times 60 \times 1 \text{ mm}$) as a working electrode, silver pseudo-reference electrode and platinum mesh counter electrode. All experimental potentials given in this work refer to silver pseudo-reference electrode system. The silver pseudo-reference electrode was calibrated against the formal potential of ferrocene / ferrocinium redox couple, whose recorded potential versus this electrode was constant, amounting to $+0.420 \text{ V}$. 0.1 M solution of tetrabutylammonium tetrafluoroborate ($\text{Bu}_4\text{N}^+\text{BF}_4^-$), Sigma-Aldrich, $>99.0\%$ electrochemical analysis grade) in acetonitrile (Sigma-Aldrich, CHROMASOLV, $>99.9\%$, HPLC grade) was used as the electrolyte medium. The concentration of **3DDP** for electropolymerisation was 10 mM . Measurements were carried out on a Metrohm-Autolab PGSTAT100N potentiostat, taking advantage of cyclic voltammetry and single and multiple step chronoamperometry controlled potential techniques.

UV-Vis-NIR spectra were registered using an Ocean Optics diode-array spectrometers set (QE65000 and NIRQuest 512). Electropolymerisation of **3DDP** was followed spectrally by recording UV-Vis spectra of the incipient polymer layer at the ITO/quartz electrode in high-speed acquisition mode. Using 50 ms integration time setting and accumulating four sequential spectra to improve the signal-to-noise ratio, an averaged spectrum was recorded every 200 ms . Taking into account the 0.1 V/s scan rate employed for electropolymerisation, this corresponds to taking spectral snapshots of the growing polymer film at 20 mV intervals.

Electron Paramagnetic Resonance (EPR) spectra were acquired using a JEOL JES FA-200 X-band spectrometer. For coupled UV-Vis-NIR-EPR spectroelectrochemical measurements, a tube cell with a flat capillary section, fulfilling the role of a window for in situ UV-Vis-NIR measurements, was used, as envisioned by Dunsch [21] and utilised in the authors' earlier works [22]. The working electrode employed in the UV-Vis-NIR-EPR measurements was an ITO coated glass slide (Precision Glass & Optics, $20 \pm 5 \Omega/\text{sq}$, $6 \times 70 \times 0.3 \text{ mm}$). Relative spin concentrations for each potential step have been obtained through manual double integration of the first derivative EPR spectrum.

3. Results and discussion

3.1 Cyclic voltammetry

Cyclic voltammetry (CV) of **3DDP** at a Pt electrode reveals an oxidation peak at 1.25 V , at which point extremely rapid polymer film formation takes place. This behaviour of the monomer is well in line with that of other 3-alkylpyrroles in this regard. The effect has been

observed both for potentiodynamic [**Error! Bookmark not defined., Error! Bookmark not defined.**] and galvanostatic [23] modes of performing electrochemical polymerisation. The maximum applied anodic potential was curtailed to the onset of monomer oxidation (1.0V), considerably decelerating the speed of electrode deposit growth. This is illustrated by **Fig 1**, wherein the evolution and development of a polymer oxidation signal at +0.2 V can be observed. Conversely, the reduction signal of the oxidised polymer film is significantly broader, indicating a hindered dedoping process. This may indicate a significant difference in conductivity between the doped and dedoped polymer. The progressive growth of the polymer redox signal demonstrates that tractable control over the polymer film yield and its thickness (**Fig. 1**) can be effected. Moreover, overoxidation of the incipient polymer is evaded, as evidenced by the steadfastness of the polymer oxidation peak potential upon accumulation of successive polymer layers. Furthermore, the evolution of a second reduction signal, with an onset at -0.4 V is observed, indicating the occurrence of another charge transfer process.

Aiming to investigate the intrinsic properties of **poly(3DDP)** films, care has been exercised to fabricate suitably thin films, so as to warrant charge transfer limited redox processes taking place in them upon redox doping. Monitoring the shape of the CV response of the incipient polymer, film deposition was run until first signs of departure of the polymer oxidation peak to higher potential values were observed. Obtained polymerisation CV curves are qualitatively comparable to those reported for 3-octadecylpyrrole [**Error! Bookmark not defined.**], but considering the charge densities, considerably thinner polymer films have been prepared by us.

Electrochemical response of the **poly(3DDP)** film (**Fig. 2**) features two, well-developed peak pairs, having formal potentials of -0.35 V and 0 V. Compared to the CV responses of poly(3-octylpyrrole) [**Error! Bookmark not defined.**], poly(3-decylpyrrole), and poly(3-hexadecylpyrrole) [**Error! Bookmark not defined.**], each electrochemical step can be clearly discerned and quantised. In the case of **poly(3DDP)**, each peak is accompanied by a distinct and reversible colour change. At the first, low-potential one, the film converts from pale yellow to violet-pink, whereas surmounting the second, high potential one, renders the film black. Direct, transmissive yellow to black, colour switching has been previously observed in polypyrrole by Diaz et al. [**Error! Bookmark not defined.**], but distinguishing two individual chromic transitions in a polypyrrole homopolymer has not been reported to date. The aforementioned, distinct colour changes clearly indicate that both CV peak pairs represent redox reactions taking place in the polymer. Consequently, each chromic state represents a unique redox state of the polymer. The redox and associated chromatic transitions of the polymer are reversible and reproducible, just as the overlapping current traces in each voltammetric cycle

are. The colour contrast, seen in **Fig. 2** photos, was found to be very sensitive to the thickness of the polymer layer, just as is the number and discernibility of its chromatic transitions. The same was observed for the separation and half-widths of CV peaks, consistent with the initial findings of Diaz et al. [Error! Bookmark not defined.].

3.2 Chronospectroelectrochemical investigation

Fast, time-resolved UV-Vis chronospectroelectrochemical study of **3DDP** polymerisation has been employed in order to optimise the polymer film thickness, so as to achieve the best chromic contrast between its coloured states. The UV-Vis spectra of the incipient polymer were acquired during the CV polymerisation process at 200 ms (20 mV) intervals (**Fig. 3a**). The resulting collection of spectra, plenteously and scrupulously depicting the development of the polymer film's spectral features, is shown in **Fig. 4**.

The progress of **poly(3DDP)** deposition is reflected in the evolution of the acquired spectra, detailing the generation and decomposition of charge carriers in the polymer layer. This claim may be exemplified by the study of the transmittance changes in the range of 450÷600 nm. The increase of applied potential induces a decrease in transmittance, followed by its increase upon reaching more positive potentials. This behaviour is explained by the formation of a semi-oxidised absorbing species and its oxidative transformation into a species absorbing in the 700÷900 nm range.

Further analysis of transmittance changes undergoing in the 450÷600 nm range shows a rapid transition occurring at 0.0 V, both in the anodic and cathodic half-cycles. This is concurrent with the voltammetric response of the **poly(3DDP)** film on the Pt flag electrode (**Fig. 2**). Interestingly, the CV curves registered during electropolymerisation on an ITO/quartz electrode (**Fig. 3a**) feature no distinct peak at this potential. This indicates that the redox process is relatively slow, which is explained by the fact that it induces significant changes in the conformation of the polymer, also accounting for the observed sharp change in transmittance. The above leads to the conclusion, that a point has been found, where the doping level of the system becomes sufficiently high to accommodate a change in the prevalent structure of the polymer chains from aromatic to quinoid.

The collected spectra, allow mechanistic conclusions to be drawn, however, they also serve to provide information as to the changes in macroscopic properties of the growing deposit. Taking the transients at selected wavelengths enables to see the changes taking place in careful detail. **Fig. 5** shows the instantaneous transmittance of the polymer film at 370 nm and 780 nm – the edges of the visible light range, and 530 nm, being the mid-energy wavelength of this

spectral region. Clearly, as the number of completed voltammetric cycles grows, the amplitude of transmittance fluctuations first increases and then gradually deteriorates.

Analysing the transmittance peaks and troughs and taking the differences of their coupled pairs, one obtains the dependence of the film optical contrast with its thickness, expressed indirectly by the number of completed electropolymerisation cycles (**Fig. 3b**). Defining the optical contrast as the difference of the maximum and minimum optical transmittance of a film layer, care needs to be exercised to correctly identify the transmittance extrema (**Fig. 5**) of progressively thicker polymer layers accumulated during electropolymerisation. Optical contrast increases for the first polymerisation cycles and clearly peaks between the fourth and fifth cycle. When further increasing the number of completed voltammetric cycles, one sees the steady decay of transmittance changes of the film, with the film becoming increasingly opaque, particularly from the tenth polymerisation cycle and onwards.

Aposing these findings with the CV of the polymer film (**Fig. 3a**) reveals that contrast is highest when the polymer still features a peak-devoid oxidation current plateau above +0.2V. This indicates that maximum optical responsiveness of the film is attained when the film redox processes are still charge transfer controlled. The oxidation peak emergence suggests that diffusion hindrance factors come to play, being either the progress of the redox propagation front in the film or the ingress of charge counterbalancing anions to it. All the above impede attainment of thermodynamic doping equilibrium, leading in effect to inhomogeneous doping of the polymer and, effectively, deterioration of the bulk optical contrast of the electrochromic film.

Acquiring snapshots of the UV-Vis spectrum at fine time intervals, colour switching dynamics of poly(3DDP) films has been investigated. Evaluating the behaviour of poly(3DDP) films using multiple double-step chronoamperometry coupled with time-resolved full spectral range UV-Vis spectroscopy, comprehensive sets of information about the full visible spectral range behaviour of the polymer film have been collected (**Fig. SI.3**), giving information about colour accommodation performance of the polymer. Taking transients to these plots at 650 nm, the chronoabsorptometric plots at different switching speeds are obtained and presented in **Fig. 6**. The plots reveal that following application of potential to the film, its principal colour switch takes place in 1 to 2 seconds time range, after which the film continues to equilibrate only. This is evident when the switch duration is shortened to 1 second. The result is a decrease of chromic contrast from almost 11% to 6%. Further decrease of switch time duration, down to 0.5 seconds, decreases the contrast value by one percent only. Irrespective of the switching rate, repeated potential stepping of poly(3DDP) yields stable and reproducible spectral response in the whole wavelength region, as seen in **Fig. SI.3**. It is interesting to note that decent symmetry of

transmittance profiles upon both forward and reverse switches is observed, indicative of unhampered oxidation and reduction of the thin poly(3DDP) film. Reduction of thicker doped conjugated polymer films is usually at issue here, being impeded by considerably worse conductivity of undoped polymer film. Layers of undoped polymer form first at the electrode/polymer film interface, and it is those poorly conducting layers that interfere with electrical contact between the electrode and polymer layers still to be dedoped, hindering the recovery of undoped polymer spectral characteristics. Besides that, the switching performance of an electrochromic polymer is governed by a number of both intrinsic and extrinsic factors, with the most prominent of the latter ones being the identity of the electrolyte salt used. Here, tetrabutylammonium cation used is rather bulky specie; hence, the kinetics of its exchange upon potential induced change of doping level of the polymer may be retarded, compared to smaller lithium or shorter chain tetraalkylammonium cations. Consequently, optimisation of the electrolyte medium should certainly afford improvement of chromic contrast of poly(3DDP) in electrochromic device application.

Summarising, the impact of the data and reasoning presented above is binary, as it both evidences a novel application of transient UV-Vis spectroelectrochemical techniques and serves to exemplify the process of preparing a thickness-optimised polymer film for high-contrast electrochromic layers. The 200 ms resolution of the in situ spectral study was found to be sufficient for characterising the electro-deposition of the incipient polymer film, as changes in the population of absorbing species are clearly distinguishable (**Fig. 5**). Furthermore, initial investigations show that this approach may also be adopted for the in situ study of polymer doping / dedoping processes.

3.3 EPR-UV-Vis-NIR spectroelectrochemistry

In order to elucidate the nature and mechanism of clearly redox driven multi-electrochromic behaviour of **poly(3DDP)**, the properties of contrast-optimised polymer films were studied by triple EPR-UV-Vis-NIR spectroelectrochemistry, results of which are presented in **Fig. 7** and **Fig. 8**.

At potentials as low as -0.6 V, ample concentration of spins was found to persist in the **poly(3DDP)** layer (**Fig. 8a**), accompanied by clear absorption bands in the NIR region (**Fig. 7a**). This indicates that the doped state of **poly(3DDP)** is still thermodynamically stable at such low potentials [**Error! Bookmark not defined.**]. However, the low conductivity of the polymer film, evidenced by small CV currents below -1.0V (**Fig. 2**), indicates that the polaron lattice comprises loosely dispersed, isolated spins.

The rise in relative spin concentration, progressing up to -0.3 V signifies electro-generation of polaronic species. This process turns out to be associable with the first chromatic state of the film, observed in the CV response of the polymer (**Fig. 2**). Upon further oxidation, the spin concentration gradually diminishes, at $+0.1$ V reaching the value observed at -0.6 V. The sharp difference in transmission spectra between the two states points to the formation of a spinless electrooxidation product. Unfaltering conductivity, manifested by the current magnitude of the polymer CV at these potentials (**Fig. 2**), indicates that additional charge carriers are generated in the polymer film, dismissing the possibility of its degradation. All this suggests that at higher potentials, bipolarons appropriate the role of prevalent charge carriers in the polymer film. Furthermore, the development of a uniform drop in transmittance (tantamount to arising broad band absorption) across the UV-Vis-NIR, is a symptom of evolution of bipolaronic energy bands responsible for the conductive polymer state. It is, therefore, those electronic transitions between the bipolaron and valence bands that afford the polymer its broad visible band absorption and, hence, its black colour.

The striking property of the **poly(3DDP)** system here, is that the doping-induced and doping-impacted bands amalgamate in a distinct way, giving levelled absorptivity across the whole visible light range, translating in turn to black colouration. Considering that such behaviour derives from both intrinsic (band positions, their absorption coefficients) and conferred (doping level, its uniformity and homogeneity accounted for by film physical properties) factors, we conclude that layer optimization plays a non-trivial role in shaping the precise colouration of the optical polymer layer. The maximum optical contrast of 14.7 % for the transition from -0.6 V to $+0.6$ V was registered at 613 nm, whereas the average contrast across the visible range was 10.4 %. These values compare favourably with other black coloured electrochromic polymers based on pyrrole (below 20% in case of **[Error! Bookmark not defined.]**), however, transmissive-to-black conjugated copolymer electrochromes have been reported to achieve optical contrasts of up to 88% in the extreme case of a polyaramides **[Error! Bookmark not defined.]**. The merit of our system lies in its chemical simplicity, which is open for further prospection across other alkyl functionalised heterocyclic systems of thiophene or selenophene.

The transmittance spectra and relative spin concentrations registered for the dedoping cycle are presented respectively in **Fig. 7b** and **Fig. 8b**. Upon decreasing the applied potential, visible range transmittance progressively increases and the signal at 392 nm returns to its original state. The behaviour of the film in the dedoping cycle begins to deviate from that in the doping cycle at -0.3 V. In contrast to the doping cycle, no spin concentration maximum is attained in the dedoping cycle. Furthermore, the transmittance spectra registered during dedoping

do not show the reconstitution of the NIR band. Instead, transmittance observed in the 460÷640 nm range is lowered in comparison to the doping cycle.

Based on the above changes, the 460÷640 nm absorption signals are considered related to polarons, whereas, the NIR band may be attributed to bipolaronic species. The evolution of these two bands, along with the 392 nm undoped polymer signal, indicates that electrochemical reduction of bipolarons may yield both polarons and the ground state polymer. The constant increase in spin concentration upon dedoping evidences high stability of the **poly(3DDP)** polaron form, even in potentials as low as -0.6 V. Such a phenomenon was expected on the grounds of the CV response of the polymer film (**Fig. 2**), wherein the reduction peak at -0.45 V extends its onset as far as -1.0 V.

The polaron lattice, obtained upon dedoping the polymer at -0.6 V appears composed of a significant number of isolated spins, hence, the low currents at the low potential end of the CV response of the polymer. Interestingly, the polymer at the beginning of the doping cycle (at -0.6 V) differs from that at the end of the dedoping cycle (at -0.6 V), both in spin concentration and optical absorption. This phenomenon has been recognised and dubbed a “closure failure effect” by Hillman et al [24] and has also been observed in our earlier work for PEDOT [25], being attributed to the charge detrapping and reorganisation of the structure of the polymer upon slow doping and dedoping.

In order to explore this effect, a third, repeated doping cycle has been performed after the aforementioned two. The relevant UV-Vis-NIR and EPR data is presented in **Fig. 7c** and **Fig. 8c** respectively. The dependence of relative spin concentration on applied potential follows the same trend as in the dedoping cycle, evidencing the repeatability and reversibility of the doping / dedoping processes in this potential range. Interestingly, upon repeated oxidation to +0.6 V, an increase in the uniformity of transmittance of the film, across the wavelength range, is observed.

The spectra, particularly those recorded for the dedoping and second doping cycles, reveal that the high energy polaron absorption signals overlap with those corresponding to the undoped polymer. The energies of these transitions are approx. 3.2 eV for the undoped polymer and 2.9 eV for the polaronic form. The low energy polaron absorption signal is found at 1.1 eV and the bipolaronic band at 2.0 eV. In conjunction with the electrochemical response of the polymer (**Fig. 2**), an interesting energy structure of the polymer is portrayed. The low oxidation potentials indicate that the valence band edge of the polymer is located at extremely high energies of approx. -3.7 eV, as calculated from the onset of the first oxidation peak of the polymer [26] (**Fig. 2**) and consistent with the electronic donor nature of polypyrroles. This is further supported by the presence of high concentrations of polaronic charge carriers at potentials as low as -1.0 V. The significant band gap of the system limits its application as a hole-

transporting layer, however, its energy structure and significant optical absorption may be harnessed in photovoltaics, particularly as materials for the development of hybrid solar cells.

4. Conclusions

Summarising, electrooxidation of **3DDP** into thin polymer films yields a multi-electrochromic material, featuring black colour at one of its fully reversible doping states. The individual chromic transitions are traced to subsequent, well discernible redox states of the polymer, the first one representing transition from a residual (isolated) to interacting polaron lattice, while the second one corresponding to the formation of a bipolaron lattice. Optimisation of the polymer film thickness enables fabrication of electrochromic layers featuring maximum and wavelength averaged contrasts of 14.7% and 10.4% respectively. All of the above make this simple, synthetically affordable polymer material, an interesting candidate for the development of transmissive-to-black electrochromic devices. Moreover, these findings demonstrate that other, classic π -conjugated homopolymers, may well unveil intriguing chromic properties upon careful tuning of their polymerisation conditions.

5. Acknowledgements

The research was supported by Polish Ministry of Science statutory financial support for young researchers BKM/508/RCh4/2013/502.

Tomasz Jarosz is a scholar supported by the “DoktoRIS – scholarship program for an innovative Silesia”, co-financed by European Union within European Social Fund.

Research presented in this work has been carried out at the Laboratory of Advanced Spectroelectrochemical Studies, established with financial contribution of the Polish National Science Centre grant no. 2011/03/D/ST5/06042.

References

- [1] G-S. Liou, H-J. Yen, Synthesis and Electrochemical Properties of Novel Aromatic Poly(amine–amide)s with Anodically Highly Stable Yellow and Blue Electrochromic Behaviors, *Macromolecules* 42 (2009) 125.
- [2] P. M. Beaujuge, S. Ellinger, J. R. Reynolds, *The donor–acceptor approach allows a black-to-transmissive switching polymeric electrochrome*, *Nature Mater.* 7 (2008) 795.
- [3] P. Shi, C. M. Amb, E. P. Knott, E. J. Thompson, D. Y. Liu, J. Mei, A. L. Dyer, J. R. Reynolds, *Broadly Absorbing Black to Transmissive Switching Electrochromic Polymers*, *Adv. Mat.* 22 (2010) 4949.
- [4] H. Shin, Y. Kim, T. Bhuvana, J. Lee, X. Yang, C. Park, E. Kim, *Color Combination of Conductive Polymers for Black Electrochromism*, *Appl. Mater. Interfaces* 4 (2012) 185.
- [5] C. Pozo-Gonzalo, J. A. Pomposoa, J. A. Alduncin, M. Salsamendi, A. I. Mikhaleva, L. B. Krivdin, B. A. Trofimov, *Orange to black electrochromic behaviour in poly(2-(2-thienyl)-1H-pyrrole) thin films*, *Electrochimica Acta* 52 (2007) 4784.
- [6] K. Kaeriyama, H. Masuda, *Synthesis of polypyrrole having an alkyl side chain*, *Brit. Polym. J.* 23 (1990) 141.
- [7] H. Masuda, S. Tanaka, K. Kaeriyama, *Electrochemical polymerization of 3-octylpyrrole*, *J. Polym. Sci. Polym. Chem.* 28 (1990) 1831.
- [8] H. Masuda, K. Kaeriyama, *Comparative study on poly(3-alkylpyrroles)*, *J. Mater. Sci.* 26 (1991) 5637.
- [9] N. Costantini, M. J. Lupton, *Infrared spectroscopic study of polaron formation in electrochemically synthesised poly(3-alkylpyrroles)*, *Phys. Chem. Chem. Phys.* 5 (2003) 749.
- [10] M. J. Gonzalez-Tejera, M. V. Garcia, E. Sanchez de la Blanca, M. I. Redondo, M. A. Raso, I. Carrillo, *Electrochemical synthesis of N-methyl and 3-methyl pyrrole perchlorate doped copolymer films*, *Thin Solid Films* 515 (2007) 6805.
- [11] N. J. L. Guernion, W. Hayes, *3- and 3,4-Substituted Pyrroles and Thiophenes and Their Corresponding Polymers - A Review*, *Curr. Org. Chem.* 8 (2004) 637.
- [12] J. Ruhe, T.A. Ezquerro, G. Wegner, *Conducting polymers from 3-alkylpyrroles*, *Makromol. Chem. Rapid Commun* 10 (1989) 103.
- [13] J. Ruhe, T.A. Ezquerro, G. Wegner, *New conducting polymers from 3-alkylpyrroles*, *Synth. Met.* 28 (1989) 177.
- [14] D. Delabouglise, J. Roncali, M. Lemaire, F. Garnier, *Control of the lipophilicity of polypyrrole by 3-alkyl substitution*, *J. Chem. Soc., Chem. Commun*, 1989, 475.
- [15] A.F. Diaz, A. Martinez, K.K. Kanazawa, M. Salmon, *Electrochemistry of some substituted pyrroles*, *J. Electroanal. Chem.*, 129 (1981) 115.
- [16] S.A. Ashraf, F. Chen, C.O. Too, G.G. Wallace, *Bulk electropolymerization of alkylpyrroles*, *Polymer* 37 (1996) 2811.
- [17] W. M. Sigmund, G. Weerasekera, C. Marestin, S. Styron, H. Zhou, M. Z. Elsabee, J. Ruhe, G. Wegner, R. S. Duran, *Polymerization of Monolayers of 3-Substituted Pyrroles*, *Langmuir* 15 (1999) 6423.
- [18] N. Costantini, S. Capaccioli, M. Geppi, G. Ruggeri, *Characterization of electrochemically synthesized alkylpyrrole intrinsically conducting polymers*, *Polym. Adv. Technol.* 11 (2000) 27.
- [19] R.C. Foitzik, A. Kaynak, J. Beckmann, F. M. Pfeffer, *Soluble poly-3-alkylpyrrole polymers on films and fabrics*, *Synth. Met* 155 (2005) 185.
- [20] R.C. Foitzik, A. Kaynak, F.M. Pfeffer, *Application of soluble poly(3-alkylpyrrole) polymers on textiles*, *Synth. Met* 156 (2006) 637.
- [21] A. Petr, L. Dunsch, A. Neudeck, *In situ uv-vis esr spectroelectrochemistry*, *J. Electroanal. Chem.* 412 (1996) 153.
- [22] T. Jarosz, P. Data, W. Domagala, W. Kuznik, K. Kotwica, M. Lapkowski, *Solubility controlled electropolymerisation and study of the impact of regioregularity on the spectroelectrochemical properties of thin films of poly(3-octylthiophenes)*, *Electrochim. Acta* 122 (2014) 66.
- [23] N. Costantini, R. Cagnolati, L. Nucci, F. Pergola, G. Ruggeri, *Electrochemical synthesis of intrinsically conducting polymers of 3-alkylpyrroles*, *Synth. Met.* 92 (1998) 139.

- [24] A.R. Hillman, S.J. Daisley, S.Bruckenstein, *Solvent effects on the electrochemical p-doping of PEDOT*, Phys.Chem.Chem.Phys. 9 (2007) 2379.
- [25] P. Berdyczko, W. Domagala, A. Czardybon, M. Lapkowski, *Long alkyl chain bearing derivatives of poly(3,4-ethylenedioxythiophene) studied by in situ EPR spectroelectrochemistry*, Synth. Met. 159 (2009) 2240.
- [26] R. Notoya, H. Hiratsuka, A. Matsuda, *Absolute electromotive force of standard ferrocene-ferricinium electrode in aqueous and non-aqueous media*, J. Res. Inst. Catalysis Hokkaido University 29 (1981) 11.

Accepted Manuscript

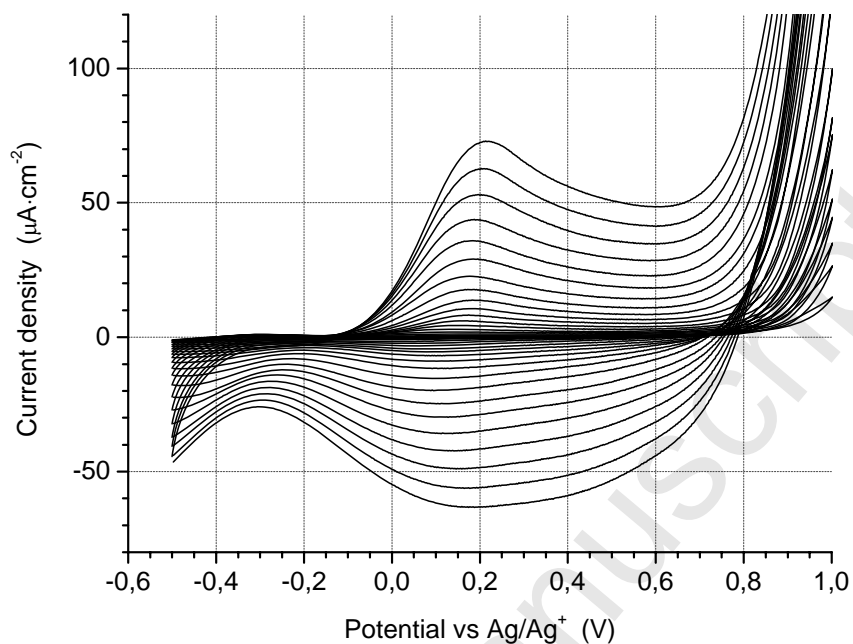


Figure 1 - Cyclic voltammogram of 10mM 3DDP in 0.1M Bu_4NBF_4 in CH_3CN at platinum flag electrode, showing progressive accumulation of an electroactive polymer deposit. Scan rate: 0.1 V/s, 20 cycles performed in total.

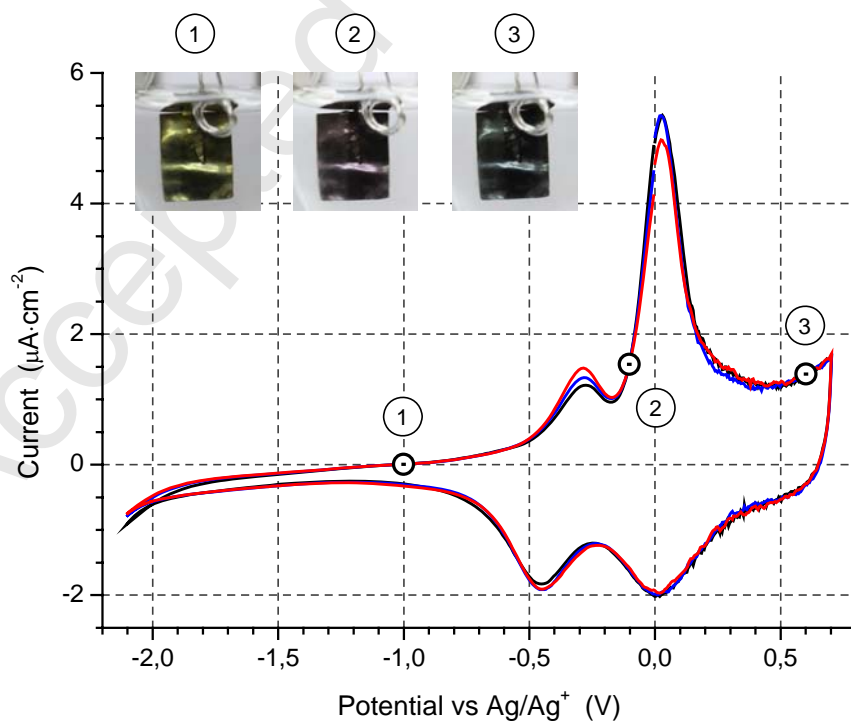


Figure 2 - Cyclic voltammogram of poly(3DDP) at Pt electrode in 0.1M Bu_4NBF_4 in CH_3CN , showing its three individual coloured states.

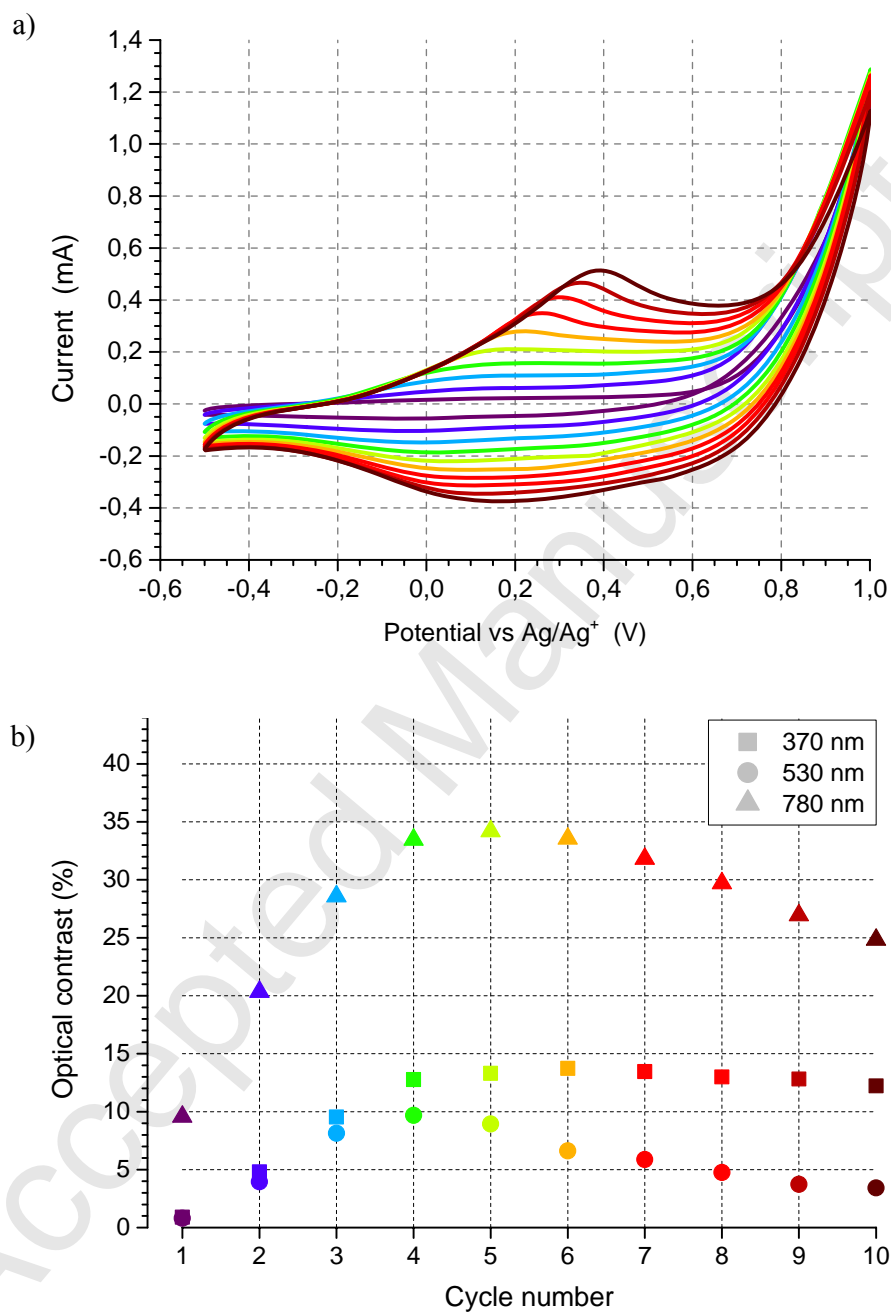


Figure 3 - a) Cyclic voltammogram of first ten cycles of electropolymerization of 3DDP at the ITO/quartz electrode. b) Optical contrast of the incipient poly(3DDP) film at selected, visible light spectrum wavelengths, measured in statu nascendi as a function of the number of completed voltammetric cycles (colour coded).

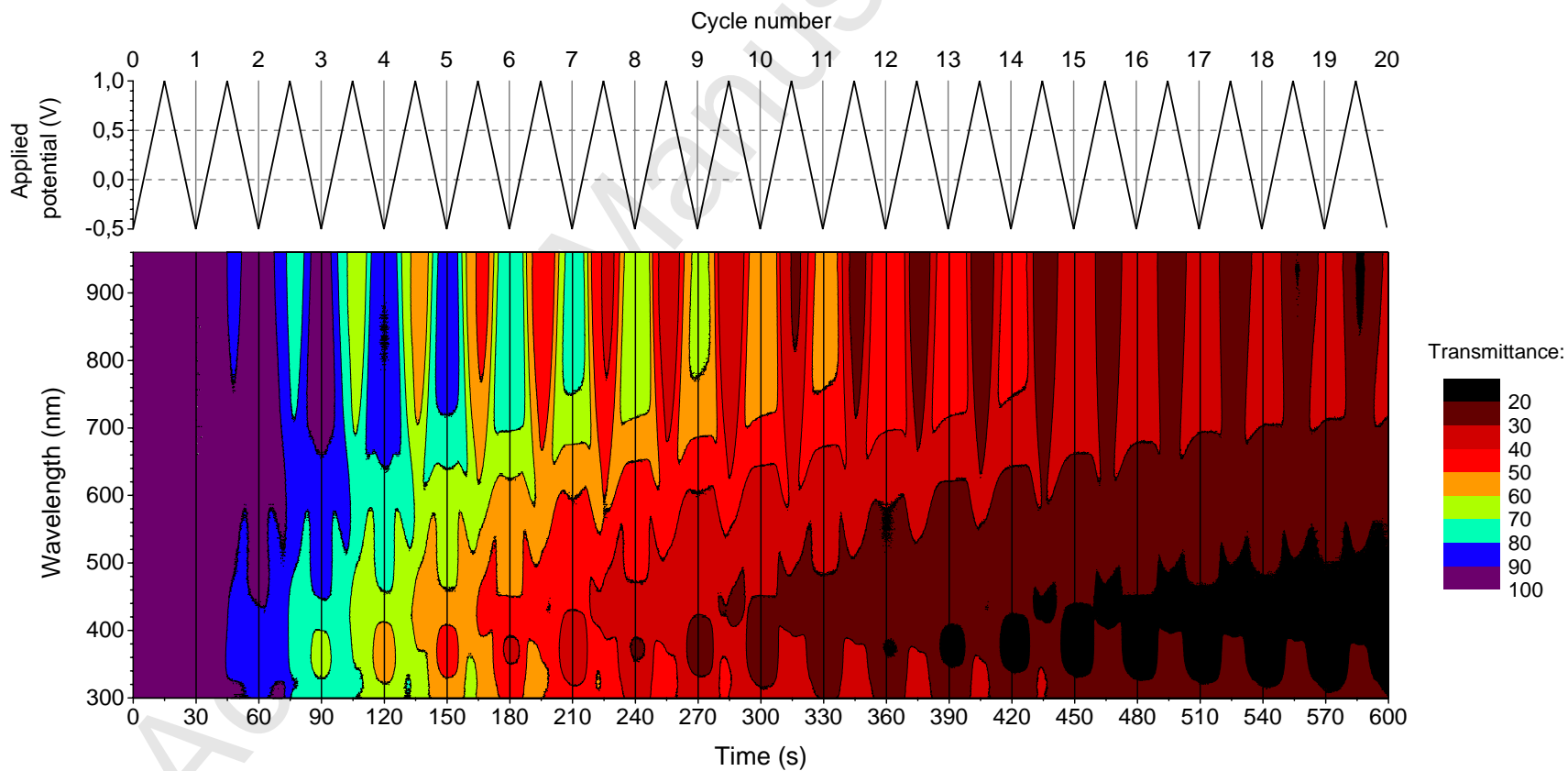


Figure 4 – Fast, time-resolved UV-Vis spectroelectrochemistry of growing poly(3-dodecylpyrrole) film. Contour plot, showing UV-Vis transmittance spectra (corrected for monomer and electrolyte absorption), registered continuously during twenty cycles of electrochemical polymerization, at an ITO/quartz electrode. Scan speed 0.1 V/s, Applied potential range -0.5 V to +1.0 V..

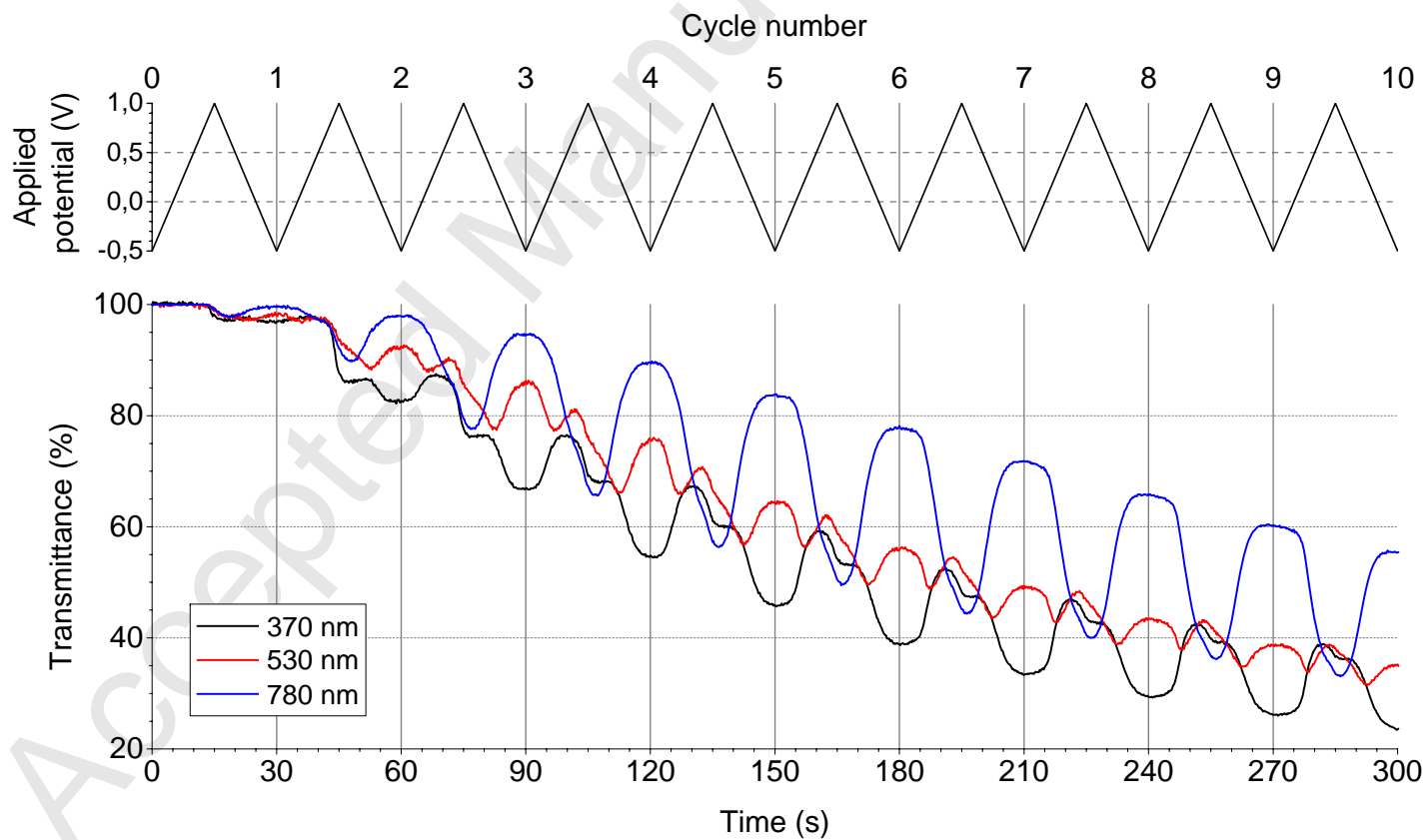


Figure 5- Time-potential profiles of optical transmittance of growing poly(3DDP) film recorded simultaneously at three selected wavelengths during the first 10 electropolymerisation cycles. Excerpt from the contour plot shown in figure 4.

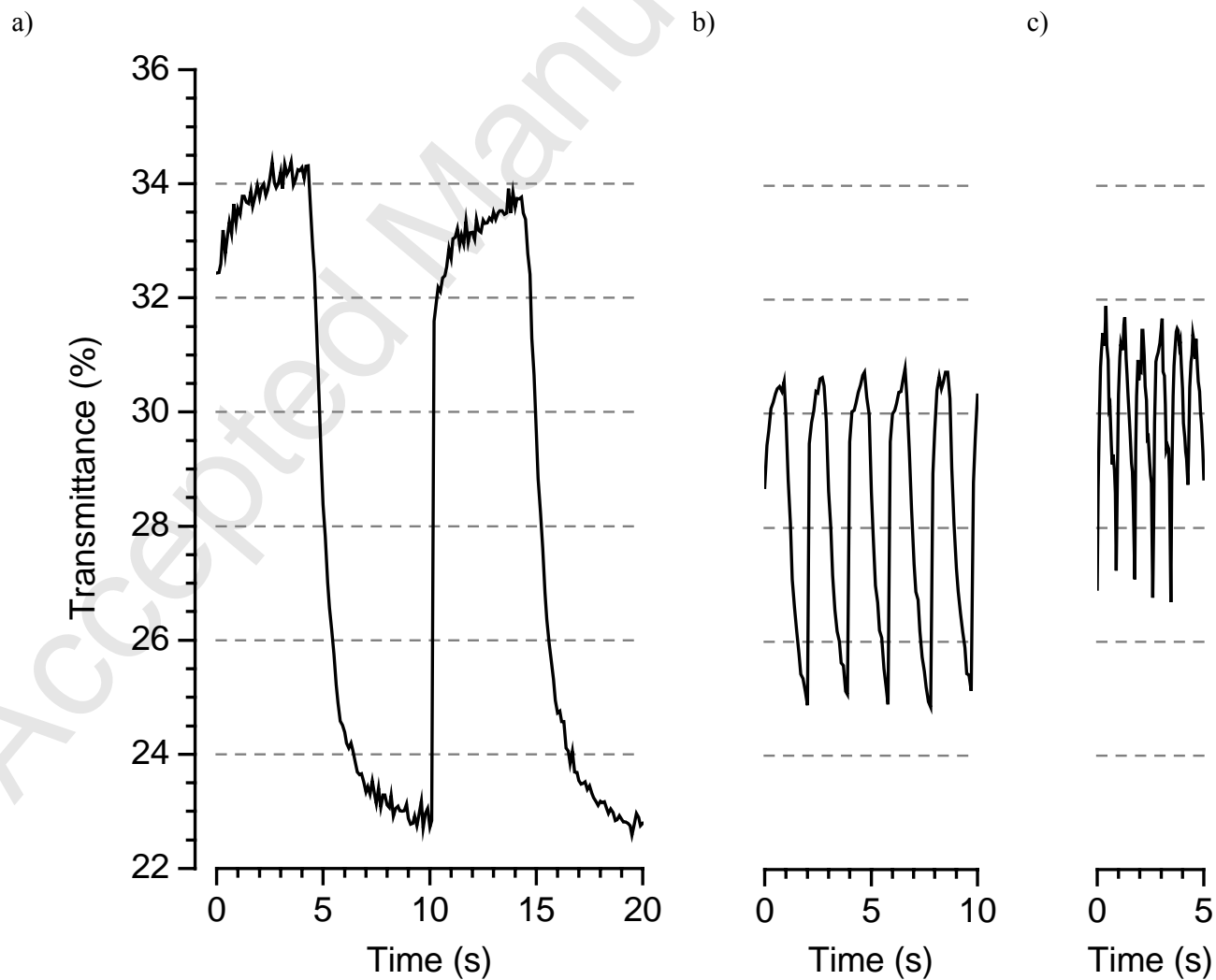


Figure 6 - Chronoabsorptometric curves of transmittance changes of poly(3DDP) film at 650nm during its repetitive, potential step switching between -0.7V (undoped) and 0.6V (doped), for potential steps of **a)** 5s, **b)** 1s, and **c)** 0.5s duration. Full spectral response of the stimulated film is presented in figure SI.3.

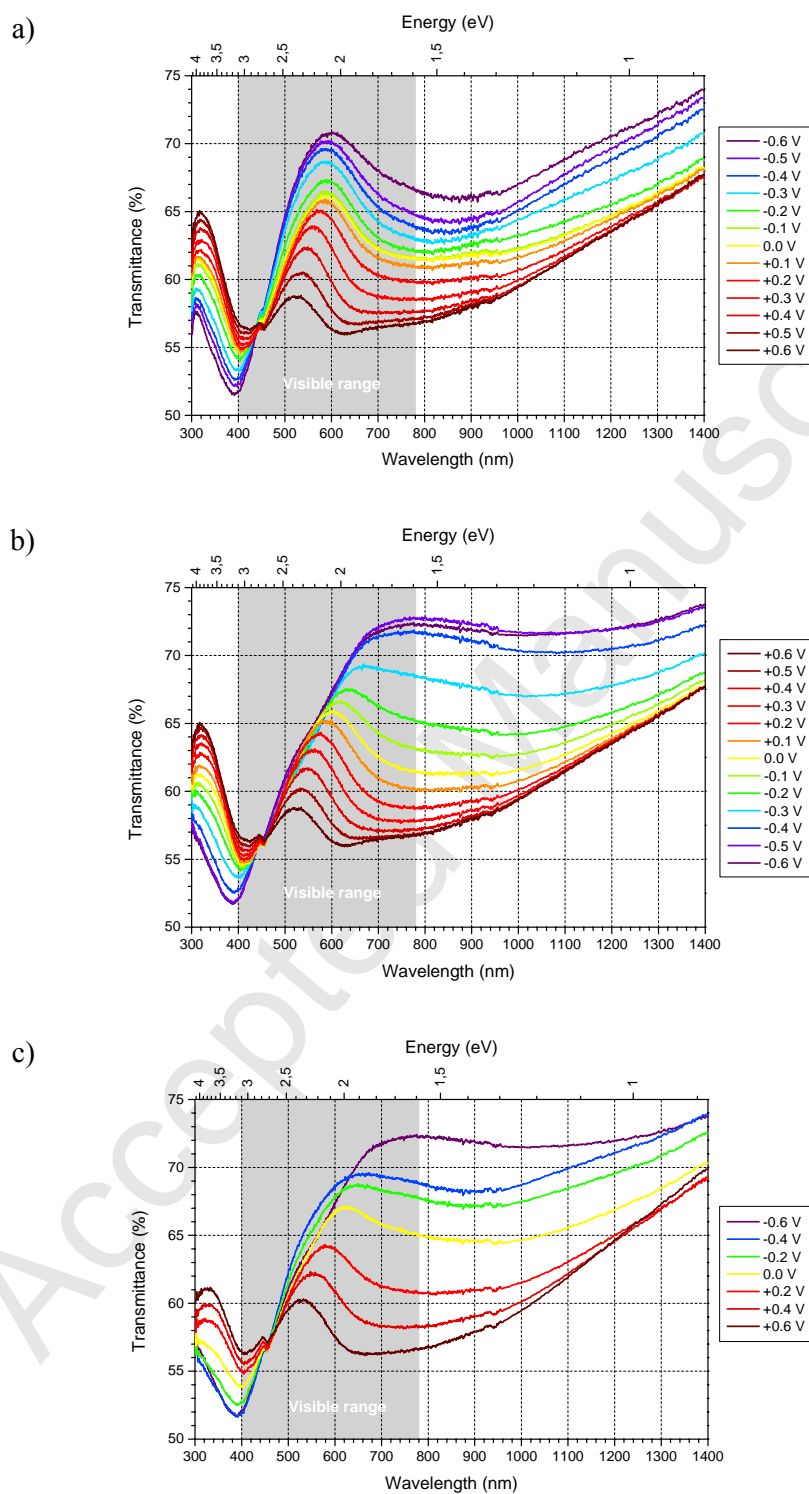


Figure 7 - UV-Vis-NIR spectra of the thickness-optimised poly(3DDP) film, registered at different applied potentials in: **a)** first oxidation (doping) half-cycle, **b)** subsequent reduction (dedoping) half-cycle, and **c)** subsequent second oxidation (re-doping) half-cycle. The spectra are colour coded to permit easy matching with

5

corresponding concentration values of paramagnetic species shown in fig. 8, registered simultaneously in an EPR-UV-Vis-NIR coupled experiment.

Accepted Manuscript

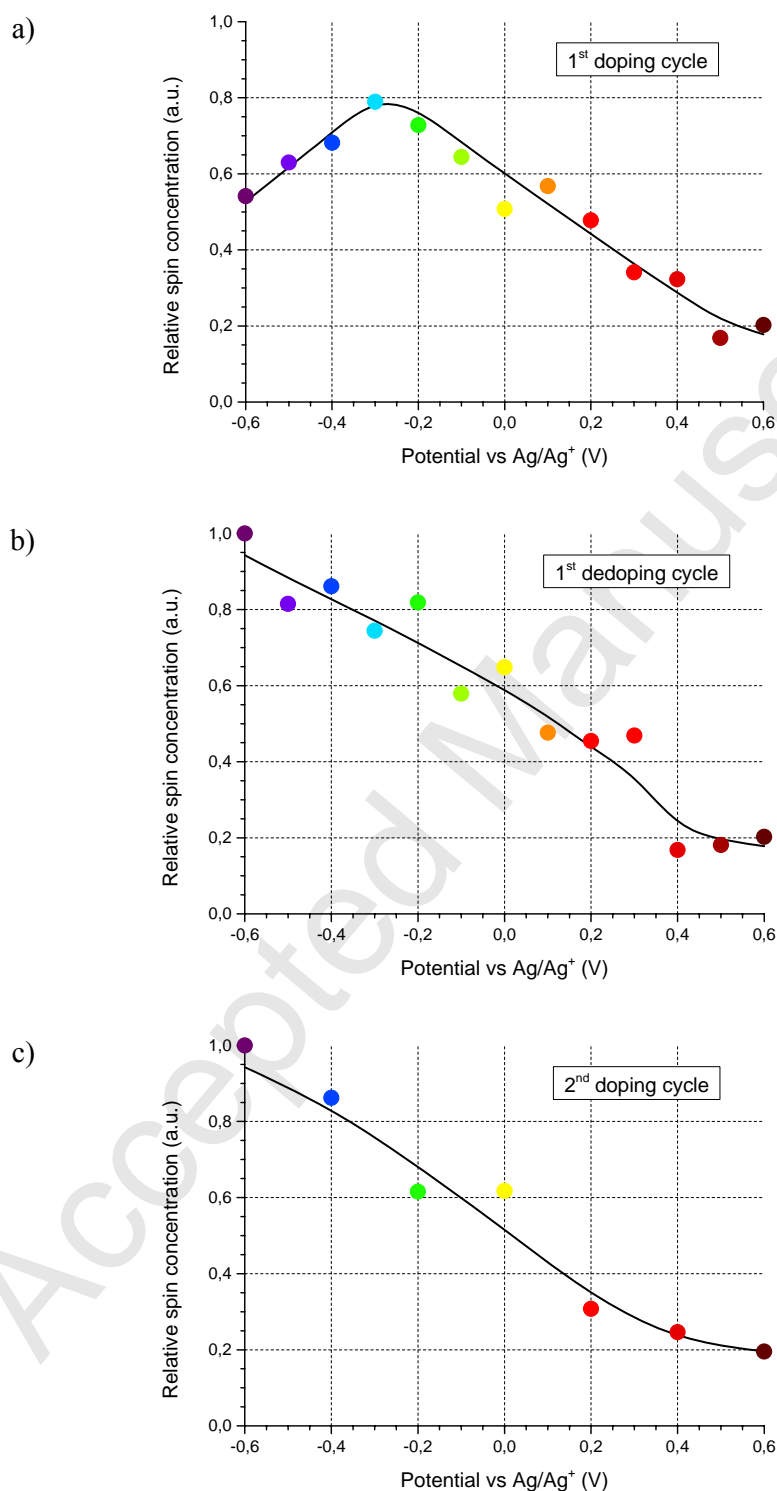


Figure 8 - Relative concentration of paramagnetic centres in the thickness-optimised poly(3DDP) film, as a function of the potential applied to it in: **a)** first oxidation (doping) half-cycle, **b)** subsequent reduction (dedoping) half-cycle, and **c)** subsequent second oxidation (re-doping) half-cycle. The spectra are colour coded to permit easy matching with corresponding UV-Vis-NIR spectra of the polymer

5

film shown in fig. 7, registered simultaneously in an EPR-UV-Vis-NIR coupled experiment.

Accepted Manuscript

Highlights

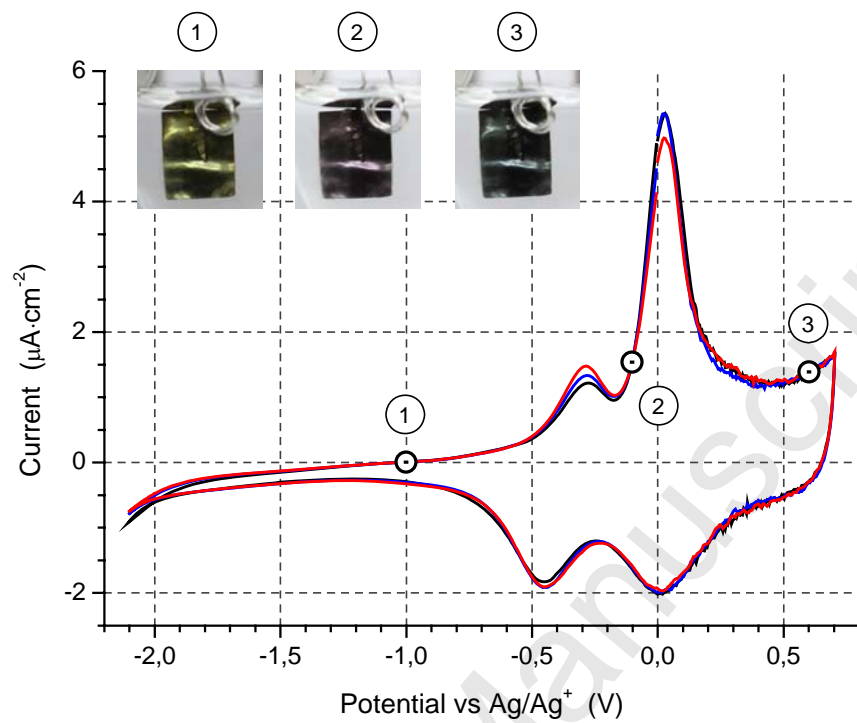
Multi-electrochromism in thin films of an alkylpyrrole derivative was observed.

Polymer film switches between yellow, violet and black.

Layer thickness optimization yields reasonable-contrast electrochromic layers.

5 Colouration is related to polymer doping states and to prevalent charge carriers.

Accepted Manuscript



5

10

