



Sensing properties of organised films based on a bithiophene derivative

M.L. Rodríguez-Méndez^{a,f,*}, C. Apetrei^b, M. Nieto^a, V. Hernandez^c, J.T. López Navarrete^c,
F. Effenberger^d, J.A. de Saja^{e,f,1}

^a Dptm. Química Inorgánica, E.T.S. Ingenieros Industriales, Paseo del Cauce s/n, University of Valladolid, 47011 Valladolid, Spain

^b Dpt. of Chemistry, Faculty of Sciences, "Dunărea de Jos" University of Galati, Galati, Romania

^c Dptm. Química Física, University of Málaga, 29071 Málaga, Spain

^d Inst. Organische Chemie der Universität Stuttgart, Stuttgart, Germany

^e Dptm. Condensed Matter Physics, Faculty of Sciences, University of de Valladolid, P^o Prado de la Magdalena s/n, 47011, Valladolid, Spain

^f Unidad Asociada FMC-UVA-Instituto de Estructura de la Materia (CSIC), Spain

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ABSTRACT

Highly reproducible optic and electrochemical sensors have been developed using organised films from a polar bithiophene derivative, the 5-(dimethylamino)-5'-nitro-2,2'-bithiophene ($\text{Me}_2\text{N-T}_2\text{-NO}_2$). The strength of the molecular dipole moment of this push-pull end-capped bithiophene has permitted to obtain highly ordered, homogeneous and reproducible films by using both the Langmuir–Blodgett and the casting techniques. The organisation of the molecules in LB films and cast films has been established by means of UV-vis, infrared and Raman spectroscopy and by AFM.

$\text{Me}_2\text{N-T}_2\text{-NO}_2$ thin films possess appealing optical and electrochemical sensing capabilities. UV-vis spectra can be modified in the presence of a variety of volatile organic compounds and the sensitivity is related to the polarity of the gas analysed. Films can also be used as electrochemical sensors because the characteristics of the current/potential curves are sensitive to the nature of the electrolytic solution. The spectral changes accompanying the applied voltage could be used to produce ionochromic sensor electrodes.

The structure of the films has an important impact in the sensing properties of the films and in their stability. The optical and electrochemical sensing properties of Langmuir–Blodgett films are more reproducible than those observed in cast films. This makes films prepared using the LB technique to be preferred as sensing devices. However the casting technique provides a fast method to obtain cheap and highly ordered sensors.

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1. Introduction

Over the last years intense research has been dedicated to the development of chemical sensors based on thiophene derivatives [1–3]. Thiophene-based sensors have been successfully utilized as the sensitive material in chemiresistors [4–5], transistors [6–7], optical [8–9], mass [10] and electrochemical sensors [11–12]. To be suitable as sensing materials, thiophenes must be able to form films compatible with microelectronics. Depending on the film forming method used, different morphologies can be obtained which have a pronounced effect on the sensing behaviour of the

devices [13]. Several techniques have been used to obtain thin films based on thiophenes. These techniques include chemical or electrochemical polymerisation [8,14], inkjet deposition [15] and Langmuir–Blodgett [16,17].

Thiophene-based oligomers have been proposed as sensitive materials because of their interesting optical and electrochemical properties and their readiness of functionalisation [18]. A variety of thiophene-based sensor materials have been synthesized by incorporating functional groups into the molecule, either along the polymer backbone or as end-capping groups [19]. Donor-acceptor end-capped derivatives are of particular interest due to the intriguing properties derived from their strong dipolar moment [20–21]. This large dipolar moment makes these thiophene derivatives good candidates for developing films with a high degree of organisation at the molecular level, facilitated by strong dipole-dipole intermolecular interactions. The 5-(dimethylamino)-5'-nitro-2,2'-bithiophene ($\text{Me}_2\text{N-T}_2\text{-NO}_2$) (Fig. 1) is a good representative of this family of compounds [22]. High values of dipole moments have been observed in all molecular conformations of $\text{Me}_2\text{N-T}_2\text{-NO}_2$

* Corresponding author at: Dpt. Química Física y Química Inorgánica, E.T.S. Ingenieros Industriales, Paseo del Cauce s/n, 47011 Valladolid, Spain.
Tel.: +34 983 423540; fax: +34 983 423310.

E-mail addresses: mluz@eis.uva.es (M.L. Rodríguez-Méndez), apetreic@ugal.ro (C. Apetrei), hernandez@uma.es (V. Hernandez), franz.effenberger@po.uni-stuttgart.de (F. Effenberger), sajasaez@fmc.uva.es (J.A. de Saja).

¹ Tel.: +34 983 423196; fax: +34 983 423192.

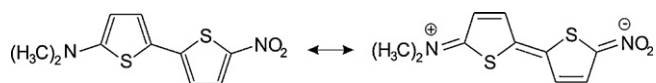


Fig. 1. Chemical structure and resonance forms of the 5-(dimethylamino)-5'-nitro-2,2'-bithiophene ($\text{Me}_2\text{N}-\text{T}_2-\text{NO}_2$).

[23]. In addition, the $\text{Me}_2\text{N}-\text{T}_2-\text{NO}_2$ possess other properties that make this compound suitable for sensing applications: $\text{Me}_2\text{N}-\text{T}_2-\text{NO}_2$ solutions possess a pronounced positive solvatochromism [22,24,25] that could be the basis of their use in optical sensors. In addition, $\text{Me}_2\text{N}-\text{T}_2-\text{NO}_2$ solutions show an interesting electrochemical behaviour [26] that could be used in voltammetric sensors.

The purpose of this work has been to evaluate the possibility of preparing ordered and reproducible thin films of $\text{Me}_2\text{N}-\text{T}_2-\text{NO}_2$ and to analyse the influence of the structure of the films in the optical and electrochemical sensing properties. For this purpose, organised films have been prepared using two different methods: the Langmuir–Blodgett technique that uses ordered monolayers formed on a gas–liquid interface to obtain organised thin films, and the cast technique where mainly intermolecular interactions determine the structure. The organisation caused by intermolecular interactions has been evaluated by means of spectroscopic and microscopic techniques. The optical and electrochemical responses in different ambiances have been tested. The influence of the structure of the films in the performance of the sensing devices has been evaluated.

2. Materials and methods

All chemical and solvents (Aldrich Chemical Ltd.) were of reagent grade and used as supplied. A donor–acceptor end-capped oligothiophene ($\text{Me}_2\text{N}-\text{T}_2-\text{NO}_2$) was synthesized according to the procedure previously described [22].

Isotherms and LB films were prepared in a KSV 5000 System 3 Langmuir–Blodgett trough equipped with a Wilhelmy plate to measure the surface pressure. The $\text{Me}_2\text{N}-\text{T}_2-\text{NO}_2$ molecules were dissolved in chloroform ($5 \times 10^{-5} \text{ mol L}^{-1}$) and spread onto ultrapure water (Millipore MilliQ), which was kept at a constant temperature of 20°C .

The surface-area isotherms were measured by compressing the floating molecules at a speed of $10 \text{ mm}^2 \text{ min}^{-1}$. At a surface pressure of 20 mN m^{-1} , the Langmuir–Blodgett films were deposited onto different types of substrates (quartz substrates, ZnS, Au, mica and ITO glass) at a substrate speed of 5 mm min^{-1} . LB films were built by Y type deposition with a transfer ratio close to 1.

Cast films were prepared by casting a drop of a $10^{-5} \text{ mol L}^{-1}$ chloroform or benzene solution of $\text{Me}_2\text{N}-\text{T}_2-\text{NO}_2$ onto the corresponding substrate.

The electronic absorption spectra were recorded with a Shimadzu UV-2101. The infrared spectra were recorded in a Nicolet Magna 760, with 4 cm^{-1} spectral resolution. Transmittance spectra were registered on films deposited onto ZnS whereas Reflection Absorption IR (RAIR) spectra were recorded on films deposited onto glass slides covered with Au at an incident angle of 80° . The gold films (500 \AA mass thickness) used as substrates were prepared by high vacuum deposition (BALZERS SCD004). FT-Raman spectra were collected by using a Bruker FRA106/S accessory fitted to a Bruker Equinox55 Fourier transform infrared absorption (FTIR) spectrometer. Data were collected in a typical backscattering configuration, and the operating power of the 1064 nm Nd:YAG laser radiation used as Raman excitation was kept at 500 mW in all the experiments. The sample was analysed as a pure solid in a sealed Raman capillary as well as in form of films deposited onto glass covered with Au. Five thousand scans with 2 cm^{-1}

spectral resolution were averaged to optimize the signal-to-noise ratio.

Films were mounted inside a 30 mL capacity gas chamber with quartz windows and exposed to vapours of benzene, chloroform hexanol and methanol. For this purpose, 2 mL of the corresponding liquid were introduced in 10 mL vials that were kept at a constant temperature (40°C) for 10 min in order to obtain a homogeneous headspace. A nitrogen flow was used as a carrier gas to drive the volatiles to the sensor chamber. The flow rate was 150 mL min^{-1} . Pulses of 2 – 15 min were performed every 20 min and UV–vis spectra were recorded immediately.

Electrochemistry was carried out in a PAR Model 263A potentiostat/galvanostat using a conventional three-electrode cell. LB films deposited on ITO glass were used as the working electrode, Pt wire as the counter electrode, and $\text{Ag|AgCl/KCl}_{\text{sat}}$ electrode as the reference electrode. KClO_4 (0.1 mol L^{-1}), KCl (0.1 mol L^{-1}) and MgCl_2 (0.1 mol L^{-1}) were used as electrolytes. A cuvette with two optical windows was used to obtain the in situ electronic absorption spectra.

AFM images of films deposited onto mica were recorded in non-contact tapping mode using a Nanoscope IIIA from Digital Instruments.

3. Results and discussion

3.1. Structural characterisation

3.1.1. Characterisation of the Langmuir films

The molecule under study formed stable and reproducible Langmuir films at the air–water interface. The π – A isotherm obtained at a fixed working temperature of 20°C and compressed at a speed of 10 mm min^{-1} is presented in Fig. 2. The surface pressure of the Langmuir films starts to rise at $7 \text{ \AA}^2/\text{molecule}$. Floating layers are stable up to pressures of 65 mN m^{-1} . The limiting area per molecule obtained by extrapolation of the slope of the low compressibility region to zero pressure is $6 \text{ \AA}^2/\text{molecule}$. Taking into account previously published structural parameters derived from crystallographic data (a face-to-face stacking distance of 3.8 \AA between bithiophene species and a side-by-side separation of 4.5 \AA) [23], it can be assumed that in the solid region of the isotherm, the molecules are arranged with their long axes perpendicular to the air–water interface. The low values of area-per molecule here observed, can also suggest that strong interactions between molecules are occurring, and formation of aggregates or multilayers is plausible.

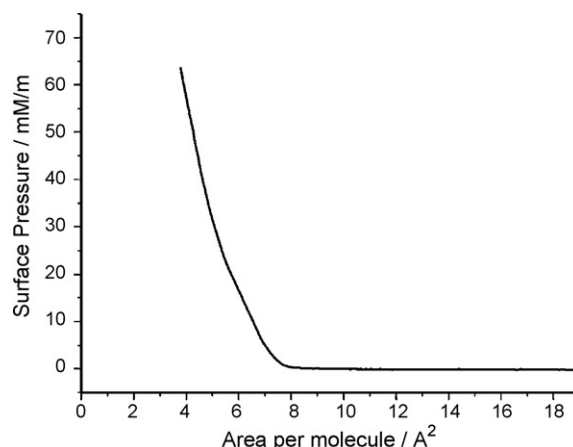


Fig. 2. Surface pressure–area isotherm for $\text{Me}_2\text{N}-\text{T}_2-\text{NO}_2$ on water at 20°C .

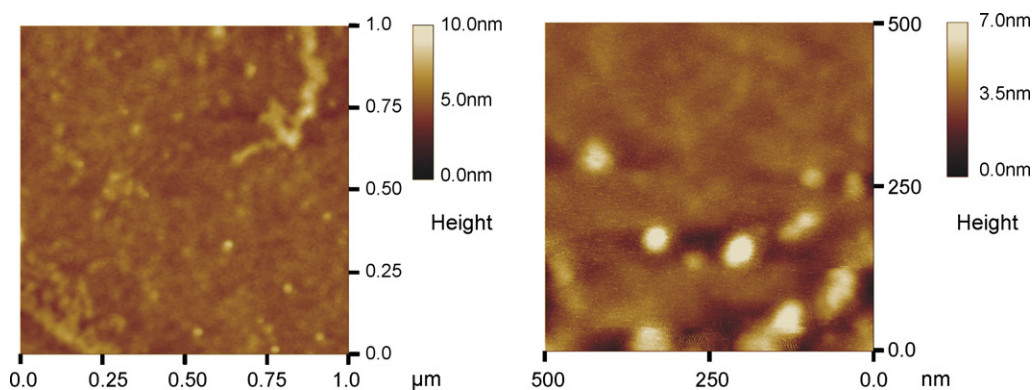


Fig. 3. AFM images registered in non-contact mode of a film deposited onto mica (left) cast film (right) 20 monolayers LB.

In order to evaluate the reproducibility of the pressure–area isotherms, experiments were recorded under different experimental conditions. It has been observed that the volume spread (500–2000 μL) or the concentration of the starting solution (10^{-4} to 10^{-6} mol L^{-1}) do not affect the shape of the isotherms. The isotherms were highly reproducible and the calculated limiting area per molecule obtained by extrapolation of the slope to zero pressure showed a variation coefficient of 0.01%.

The floating layers were easily transferred to different substrates with Y type deposition and a transfer ratio close to 1.

3.1.2. AFM characterisation

The topography images of the cast and LB films deposited onto mica are illustrated in Fig. 3. The surface of both films was smooth and quite homogeneous. Only, some differences could be observed in the roughness of the surfaces. While cast films showed a root-mean-square roughness R_q of 0.538 nm, the R_q measured for a 20 monolayers LB films was 0.394 nm. In order to investigate the reasons of the different roughness, the organisation of the films was studied in detail using spectroscopic techniques.

3.1.3. UV–vis spectroscopy of Langmuir–Blodgett (LB) films and cast films

The electronic absorption spectrum of a diluted chloroform solution of $\text{Me}_2\text{N-T}_2\text{-NO}_2$ shows one intense band at 530 nm (Fig. 4a) [25]. This band split up into two components (blue and red shifted bands) when passing from solution to films (Fig. 4b and c). This behaviour can be explained in terms of molecular exciton coupling theory (i.e., coupling of transition moments of the constituent molecules) and is consistent with a Davydov splitting which can be observed in films with a high organisation in which more than one equivalent molecular units are present per unit cell [27–28].

In the case of LB films, the sharp and intense band (at 446 nm) hypsochromically shifted from the band corresponding to the monomeric species (530 nm in chloroform) is characteristic of the

formation of a plane-to-plane stacking of the chromophores (*H aggregates*) [29]. The sharpness of the band points towards well defined intermolecular interactions. The spectrum also shows a strong and broad absorption peak (at 556 nm) shifted to the red from the transition observed in solution. Such a shift to lower energies is characteristic of head-to-tail arrangement of transition dipoles (*J aggregates*).

The electronic absorption spectra of cast films prepared from a chloroform solution also showed two bands (438 and 554 nm) associated with a Davydov splitting. The high values of dipole moments for all molecular conformations of $\text{Me}_2\text{N-T}_2\text{-NO}_2$ can explain the spontaneous organisation of the molecules in the cast films. This observation is consistent with the auto-organisation capabilities that have been observed in other thiophene derivatives [30,31]. The Davydov splitting has also been observed in films prepared from other solvents.

Although thin films obtained by the LB and the casting technique are highly ordered, some differences in the organisation can be derived from the UV–vis spectra. The bands associated to *H* and *J aggregates* are better resolved in cast films than in LB films. In cast films the red and blue shifted peaks are almost completely separated and a decrease of the relative intensity of the absorption at 530 nm is observed. This indicates that deposition by casting facilitates the interactions between monomers to reorganise in *H* and *J aggregates* in more extent than the LB technique (where the red and blue shifted peaks are not perfectly resolved because a certain amount of molecules remain in the monomeric form). However, the red shift of *J aggregates* is more pronounced in LB films indicating a spatially more extended coupling of chromophores in the same relative orientation [29].

3.1.4. Vibrational spectroscopy: FT–Raman, FTIR and RAIR

The FT–Raman spectra of LB films (20 layers) and cast films of $\text{Me}_2\text{N-T}_2\text{-NO}_2$, are dominated by 5 intense peaks at 1274, 1216, 1135, 1023 and 802 cm^{-1} . The simplicity of the Raman spectra can

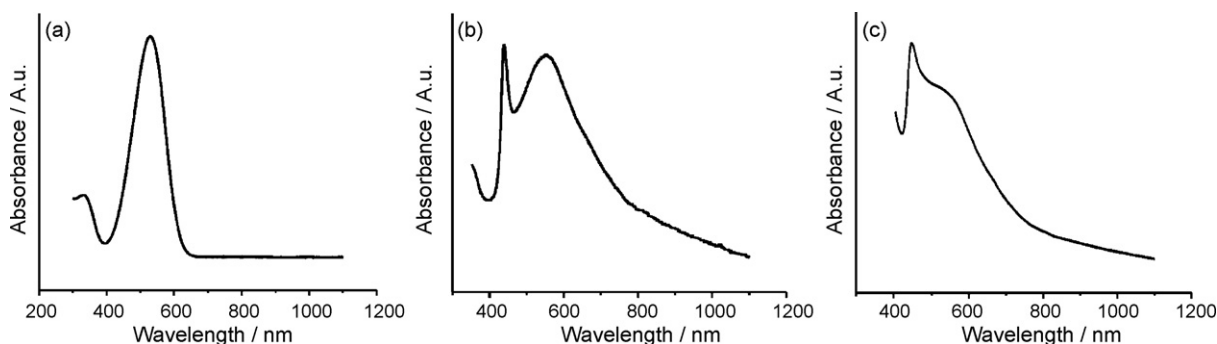


Fig. 4. Electronic absorption spectra of $\text{Me}_2\text{N-T}_2\text{-NO}_2$ (a) 10^{-5} mol L^{-1} chloroform solution; (b) cast film from a 10^{-5} mol L^{-1} chloroform solution; and (c) LB film (20 layers).

be explained through the effective conjugation coordinate (ECC) theory that justifies the appearance of a few strong Raman bands associated to particular stretching vibrations that display intensities much stronger than most of the Raman-active normal modes. In both types of films the peaks appear slightly bathochromically shifted with respect to the calculated spectra for a single molecule under vacuum. The position of the bands does not vary significantly from pellets [26,32] to LB films indicating that the molecules are stable at the water subphase and that the LB films are physisorbed onto the substrate.

Infrared spectroscopy is a powerful tool to determine the molecular alignment in thin films [33]. In the transmission spectra (TIR), the intensities of the fundamental vibrations with transition dipole component parallel to the surface are enhanced. In contrast, the RAIR selectively enhances those vibrations with a transition dipole component perpendicular to the surface. In order to probe the molecular orientation in the films, TIR spectra of LB multilayers and cast films (deposited onto ZnS) were compared with RAIR spectra of both types of films (deposited onto Au surface). In addition, the Infrared spectrum of a KBr pellet (a random distribution of molecular orientations where all the active vibrations can be observed) of $\text{Me}_2\text{N-T}_2\text{-NO}_2$ was recorded as a reference. FTIR spectra of cast and LB films of $\text{Me}_2\text{N-T}_2\text{-NO}_2$ are presented in Fig. 5. Table 1 shows a list of the active vibrations and their relative intensities in the different films and in the KBr pellet. The spectrum shows that some vibrations split into two components associated to the two structural environments that coexist in the molecule (one molecular domain associated to the thienyl ring attached to the donor group and a second domain related to the thienyl ring attached to the acceptor group).

The molecular orientation of the films was established by comparing the spectra of the KBr pellet with the TIR and the RAIR of the films. The bands in the FTIR spectrum associated to out-of-plane vibrations at 727, 736 and 774 cm^{-1} are particularly important for the discussion of the molecular orientation. In particular, the vibration at 736 cm^{-1} is assigned to the $\gamma\text{-C-H}$ bending associated to the thiophene ring bonded to the dimethyl amino group. The peak at 774 cm^{-1} is due to the $\gamma\text{-C-H}$ bending associated to the thiophene

linked to the nitro group. If the edge-on organisation proposed for the Langmuir layers was preserved during transfer, the out-of-plane $\gamma\text{-C-H}$ bendings at 727, 736 and 774 cm^{-1} should be intense in the transmission spectrum and very weak in the RAIR spectrum.

As a matter of fact, the $\gamma\text{-C-H}$ bendings appear as the most intense peaks in the transmission spectrum (Fig. 5a) and disappear completely in the RAIR spectra of the LB film (Fig. 5b). It can be concluded that the transition dipole moment of the bending vibrations is parallel to the surface and the bithiophene skeleton would be in a perpendicular arrangement in the ordered LB films.

The orientation of the cores of the molecules in the LB films can be confirmed by observing in-plane vibrations such as the band at 1331 cm^{-1} and the band at 1530 cm^{-1} which are associated to the thiophene stretching. More specifically, the band at 1331 cm^{-1} is mainly due to a mixture of the symmetric $\nu_{\text{sym}}(\text{NO}_2)$ stretching of the acceptor group with the in-phase stretching of the two ends CMe-N bonds. In turn, the band at 1530 cm^{-1} is due to a (C=C) stretching, along the two C=C bonds of each thienyl ring. As stated above, in the RAIR experimental geometry, the electric field component of the exciting beam is perpendicular to the substrate and an edge-on organisation would increase the intensity of these vibrations, as it actually occurs.

In the case of the cast films, the intensity of the vibrations corresponding to the $\gamma\text{-C-H}$ bendings are observed in the RAIR spectra with a much lower relative intensity than in the KBr pellets or the transmission spectra, but they do not disappear completely (see relative intensity values in Table 1). Taking into account the statistic character of the FTIR technique, this result indicates that the cores of the molecules also have a preferential orientation perpendicular to the substrate; however, the molecules have a degree of tilting with respect to the plane of the substrate. The analysis of the relative intensities of the main in-plane vibrational modes in the case of the cast films also reveals an edge-on molecular organisation of the cores.

Some other interesting differences are observed between the infrared spectra of LB films and cast films, which are related to the vibrations associated to the stretchings of the conjugated skeleton (vibrations above 1400 cm^{-1}). For instance, in LB films a band

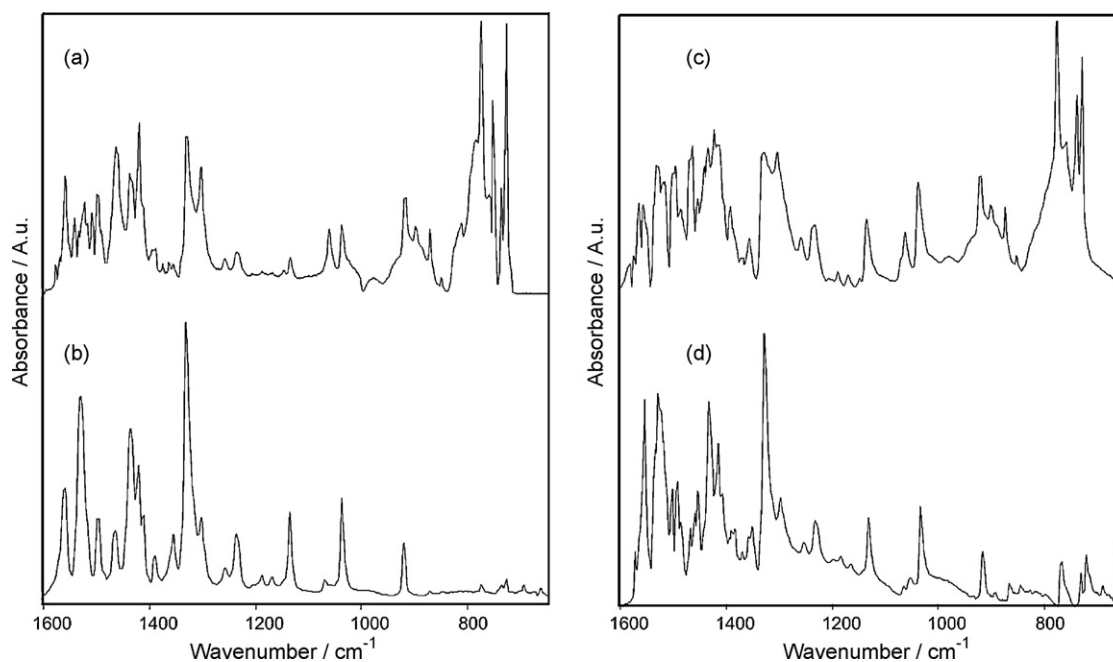


Fig. 5. FTIR spectra of $\text{Me}_2\text{N-T}_2\text{-NO}_2$ LB films (left) and cast films (right). The upper traces correspond to Transmission spectra (a) and (c) of films deposited on ZnS; the lower traces correspond to RAIR spectra (b) and (d) of films deposited onto Au.

Table 1
Infrared active vibrations of Me₂N–T₂–NO₂.

| KBr pellet | | FTIR cast film | | | | FTIR LB film | | | |
|--------------------------------|----------------|--------------------------------|----------------|--------------------------------|----------------|--------------------------------|----------------|--------------------------------|----------------|
| Transmission | | Transmission | | RAIRS | | Transmission | | RAIRS | |
| Wavenumber (cm ⁻¹) | Abs. intensity | Wavenumber (cm ⁻¹) | Abs. intensity | Wavenumber (cm ⁻¹) | Abs. intensity | Wavenumber (cm ⁻¹) | Abs. intensity | Wavenumber (cm ⁻¹) | Abs. intensity |
| | | | | 668 | 0.4 | | | | |
| 727 | 0.80 | 727 | 1.8 | 725 | 0.4 | 727 | 1.92 | 727 | 0.1 |
| 736 | 0.77 | 736 | 1.6 | 734 | 0.25 | 736 | 0.88 | | |
| | | 751 (sh) | 1.1 | | | 751 | 1.47 | | |
| 774 | 0.77 | 774 | 2 | 772 | 0.34 | 774 | 1.81 | 774 | 0.8 |
| | | | | 812 | 0.4 | 812 | 0.4 | | |
| 871 | 0.26 | 871 | 0.6 | 867 | 0.17 | 871 | 0.83 | | |
| 899 | 0.23 | 898 | 0.6 | | | 898 | 0.85 | | |
| 918 | 0.63 | 918 | 0.85 | 920 | 0.41 | 919 | 1.08 | 920 | 0.3 |
| 1033 | 1.06 | 1035 | 0.8 | 1037 | 0.74 | 1037 | 0.65 | 1037 | 0.6 |
| 1061 | 0.44 | 1060 | 0.45 | | | 1060 | 0.31 | | |
| 1131 | 1.08 | 1140 | 0.55 | 1136 | 0.65 | 1140 | 0.30 | 1135 | 0.55 |
| 1168 | 0.47 | | | | | | | 1169 | 0.12 |
| 1188 | 0.52 | | | | | | | 1188 | 0.12 |
| 1229 | 1.24 | 1235 | 0.5 | 1236 | 0.63 | 1235 | 0.46 | 1236 | 0.56 |
| 1257 | 0.80 | | | 1258 | 0.47 | 1259 | 0.42 | 1258 | 0.2 |
| 1292 | 1.93 | 1302 | 1.05 | 1301 | 0.8 | 1302 | 1.01 | 1302 | 0.6 |
| 1329 | 1.44 | 1328 | 1.05 | 1331 | 2 | 1329 | 1.22 | 1331 | 2 |
| 1354 | 0.34 | | | 1354 | 0.6 | 1362 | 0.4 | 1355 | 0.5 |
| 1390 | 0.61 | 1390 | 0.6 | 1387 | 0.58 | 1389 | 0.49 | 1390 | 0.3 |
| 1415 | 1.31 | 1421 | 1.2 | 1419 | 1.2 | 1419 | 1.3 | 1421 | 1 |
| 1428 | 0.96 | 1432 | 1.08 | 1436 | 1.5 | 1436 | 0.97 | 1435 | 1.35 |
| 1462 | 0.67 | 1462 | 0.7 | 1456 (sh 1464) | 0.85(0.6) | 1463 | 1.14 | 1465 | 0.6 |
| 1494 | 0.80 | 1494 | 0.9 | 1497 | 0.9 | 1497 | 0.85 | 1497 | 0.6 |
| | | 1514 | 0.8 | 1506 | 0.85 | 1507 | 0.72 | | |
| 1518 | 1.06 | 1528 | 0.92 | 1532 | 1.58 | 1522 | 0.79 | 1530 | 1.75 |
| 1556 | 0.51 | 1554 | 0.7 | | | 1541 | 0.68 | | |
| | | 1562 | 0.7 | 1558 | 1.50 | 1559 | 0.98 | 1560 | 0.95 |

of medium-low intensity is observed at 1497 cm⁻¹ associated to $\nu_{\text{asym}}(\text{C}=\text{C})$ motions of the thienyl rings coupled with the asymmetric stretching of the NO₂ group. This band appears with a double peak structure in cast films (1497 and 1506 cm⁻¹). Such splittings indicate a lower organisation in cast films than in LB films.

Under the light of the results obtained using UV–vis and vibrational spectroscopy, it can be concluded that both LB films and cast films are highly ordered. However, the molecular arrangement is somehow different in both types of films. The differences in the organisation can be of a key importance, since the aggregation pattern of these π -conjugated oligomers can determine the properties or the performance of a sensing device.

3.2. Sensing properties: influence of the structure

3.2.1. Optical sensors

As stated above, the Me₂N–T₂–NO₂ solutions show an intense solvatochromism (absorption maxima appear at 509 nm in chloroform solutions and shifts to 530 nm in benzene solutions). In this work, the solvatochromic effect has been used to construct optical sensors based on Me₂N–T₂–NO₂ films.

As observed in Fig. 6, the exposure of the films to vapours of benzene, chloroform, hexanol or methanol produced changes in the relative intensity of the red-shifted absorption band. The variations in intensity were linearly related to the polarity of the vapours (see inset of Fig. 6). All changes were reversible, upon nitrogen purging and the original spectra were recovered few minutes later. These results indicate that the degree of intramolecular charge transfer of Me₂N–T₂–NO₂ can be modified by changing the polarity of the surrounding atmosphere.

The absorbance changes were relative to the vapour concentration over the sensor. This is illustrated in Fig. 7 where the responses towards increasing concentrations of acetic acid are shown. The inset shows the variation of the absorbance with the time.

At low concentrations of acetic acid, the absorbance of the peak associated to *J aggregates* increased linearly with the vapour concentration. This result was in good agreement with results observed for other bithiophenes [9]. At large exposure times, protonation caused a drastic increase of the relative intensity of this band and the linearity was lost. Also in this case, the original spectrum was recovered few minutes later. Films were also sensitive towards electron acceptor gases such as NO_x (Fig. 8a). In this case, the intensity of the band associated to *J aggregates* decreased its intensity while the original band at 550 nm (corresponding to the monomer) increased its intensity. This indicates that oxidation broke the interactions between molecules and *H* and *J aggregates* disappear partially in favour of the monomeric form. In contrast, the exposure to electron donor gases such as ammonia

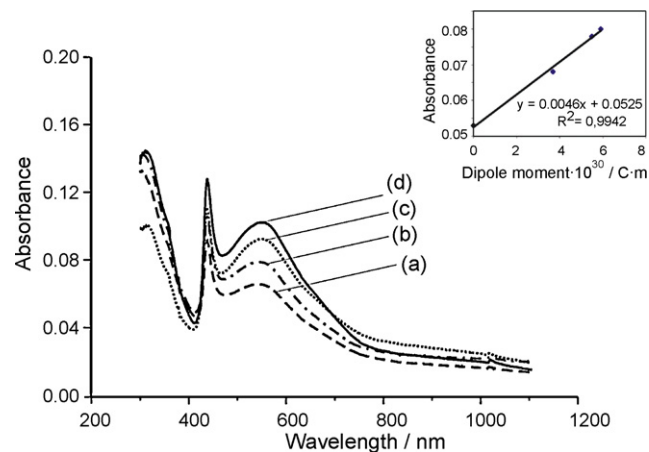


Fig. 6. Electronic absorption spectra of Me₂N–T₂–NO₂ cast film from a 10⁻⁵ mol L⁻¹ chloroform exposed to vapours of (a) benzene; (b) chloroform; (c) hexanol and (d) methanol. The inset shows the variation of the absorbance with the polarity.

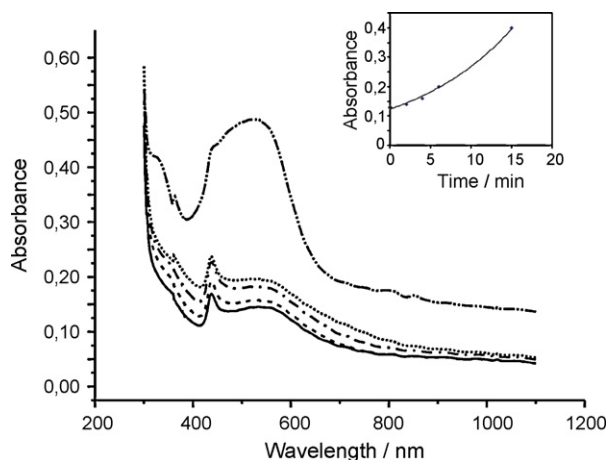


Fig. 7. UV-vis spectra of a of $\text{Me}_2\text{N-T}_2\text{-NO}_2$ cast film before (—) and after exposure to pulses of 2 (---), 4 (· · ·), 6 (— · —) and 15 (— · —) min of acetic acid. The inset shows the variation of the absorbance with the exposure time.

did not produce significant changes in the UV-vis spectra of the films.

The spectral patterns of LB and cast films exposed to vapours were quite similar, but some differences could be observed. One important difference was related with the reproducibility of the sensors. The LB technique allows preparing thin films with a controlled thickness. In LB films, the variation coefficient of the absorbance measured at 556 nm in 10 films (20 monolayers) was of a 4%. In contrast, using the casting technique, the thickness can be hardly controlled. The absorbance showed higher variability with a variation coefficient of a 15%. On the other hand, the responses of LB films to ten consecutive pulses of VOCs were more reproducible than those observed in cast films (variation coefficient of 5% in LB films and of 10% in cast films).

3.2.2. Electrochemical sensors

Polythiophenes have been used as the sensing materials in a variety of electrochemical sensors, including amperometric gas sensors [34]. Our purpose in this work is to evaluate the possibility of using these films as voltammetric sensors. In chemically modified voltammetric sensors the redox transformations of the polymeric material deposited onto the electrode are accompanied by ion movements between the solution and the bulk material. This diffusion is necessary to preserve the macroscopic electroneutrality of the electrode. For this reason, the voltages of the peaks observed in the voltammograms and their intensity depend on the nature and the concentration of the ions solved in the test solution. The

electrochemical responses can then be used to detect ions present in the solution [35].

Experiments were carried out to evaluate the sensing capabilities of $\text{Me}_2\text{N-T}_2\text{-NO}_2$ films. Cyclic voltammograms of LB (20 layers) and cast films of $\text{Me}_2\text{N-T}_2\text{-NO}_2$ deposited on ITO glass were recorded in contact with 0.1 mol L^{-1} KCl. Experiments were carried out, from -0.9 to $+1.3 \text{ V}$ at a scan rate of 0.1 V s^{-1} . The cyclic voltammograms corresponding to fresh films are shown in Fig. 9a and b. The voltammograms of nanostructured cast films (Fig. 9a) show a broad and intense anodic peak at 0.92 V . This peak is accompanied by one anodic wave at 0.55 V . A quasireversible redox pair of very small intensity appears at $E_{1/2}$ of 0.1 V . In addition, an irreversible cathodic wave is observed at -0.68 V with a shoulder at -0.75 V . According to the literature, the weak redox pair at $E_{1/2}$ of 0.1 V and the irreversible cathodic wave at negative potentials (at -0.78 V) would correspond to the reduction of hydroxylamine and the irreversible formation of the radical anion respectively [36]. The intense and broad peak at 0.92 V can be associated to the formation of the radical cation of $\text{Me}_2\text{N-T}_2\text{-NO}_2$. According to the UV-vis spectra, the broadness of the peak is due to the existence of molecules with different molecular surroundings. Cyclic voltammograms of LB films show the same general behaviour, with a broad band at ca. 0.86 V . In this case the three molecular surroundings (monomers, *H* and *J* aggregates) can be clearly observed and appear as shoulders at 0.76 , 0.87 and 1.02 V (Fig. 9b).

The first cycle differs from the subsequent ones. Upon successive cycling, peaks shift to lower potentials, and overlapped peaks are resolved. After the third cycle, reproducible voltammograms were obtained (Fig. 9c and d). This phenomenon is common in electrochemistry and is related to the diffusion of ions inside the film necessary to maintain the electroneutrality [19]. Usually, thin films need few cycles to establish a smooth diffusion of ions inside the film. In addition, diffusion can cause a reorganisation of the molecular interactions that modify the structure of the films. The broad peak observed in the first cycle using the LB film, splits into two well resolved peaks (at 0.8 and 0.68 V) evidencing the existence of molecules with two different surroundings (Fig. 9d). In cast films reorganisation of the structure is more important and produces voltammograms where only one intense anodic wave at ca. 0.68 V is observed accompanied by a small shoulder at 0.81 V (Fig. 9c). The stability of cast films was lower than that of LB films. After several cycles, voltammograms obtained from cast films lost their signals. In contrast, LB films could be cycled up to 50 times without important losses of the intensity of the signals.

The films were sensitive to the nature of the ions present in the electrolytic solution. The electrochemical response of the films immersed in MgCl_2 was similar to those recorded in KCl. The similar behaviour in both solutions allows concluding that during oxidation–reduction process, anions (instead of cations) diffuse

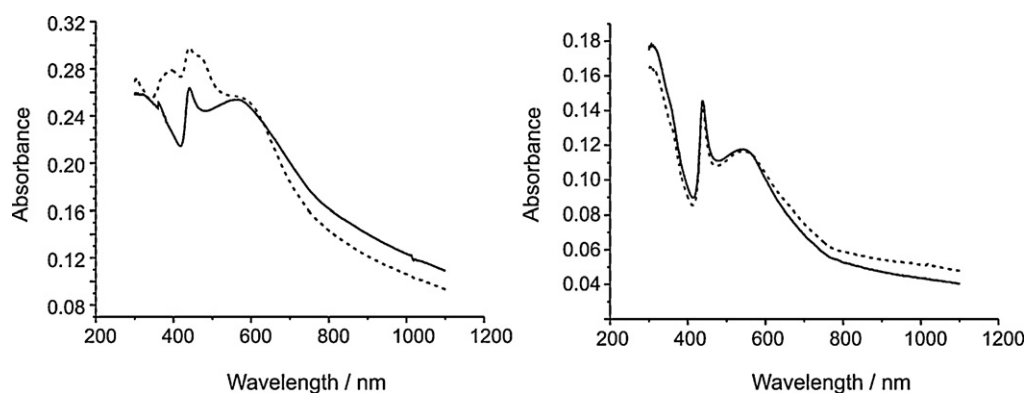


Fig. 8. UV-vis spectra of a of $\text{Me}_2\text{N-T}_2\text{-NO}_2$ cast film before (solid line) and after (dotted line) a 2 min pulse of NO_x (left) and NH_3 (right).

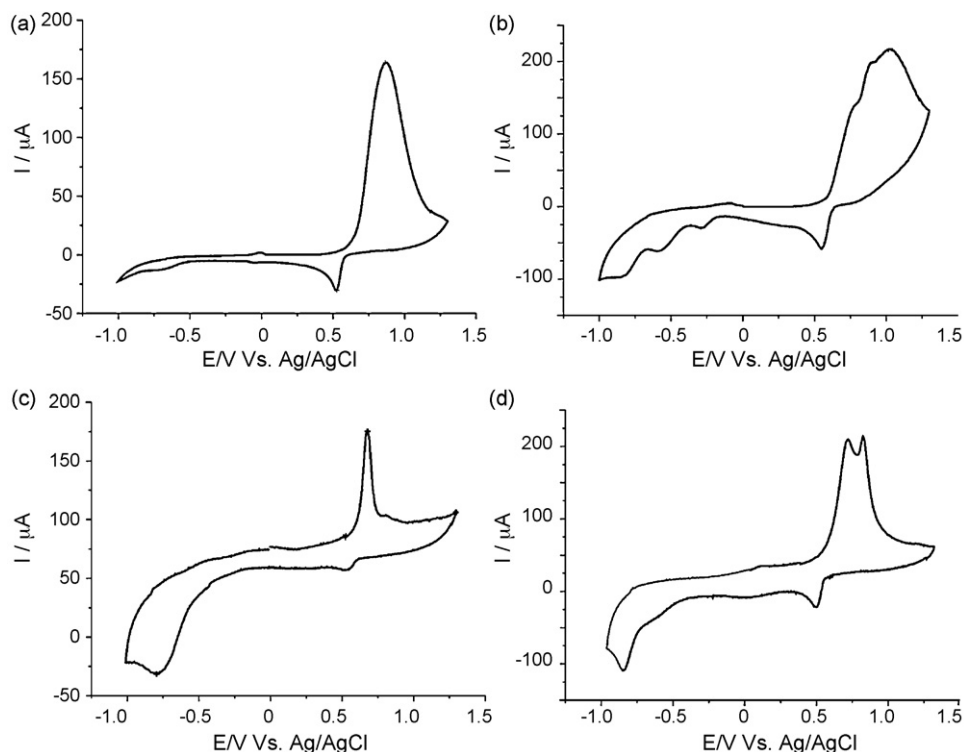


Fig. 9. Cyclic voltammogram of thin films of $\text{Me}_2\text{N-T}_2\text{-NO}_2$ deposited onto ITO glass and immersed in 0.1 mol L^{-1} KCl (a and c) cast films (b and d) 20-layer LB film. Upper traces correspond to the first scan. Lower traces correspond to the fifth scan.

inside the films to maintain the electroneutrality. According to this assessment, voltammograms registered in KClO_4 differ from those observed in KCl and after three cycles, only one broad anodic wave at positive potentials was observed in both LB and cast films (Fig. 10). In addition, the presence of KClO_4 facilitates the oxidation of the $\text{Me}_2\text{N-T}_2\text{-NO}_2$ and the anodic waves appear shifted to lower (from 0.92 V in cast films to 0.82 V in KClO_4). According to these results, films prepared using the LB technique can be used to detect the presence of anions in aqueous solutions.

π -Conjugated polymers, e.g. polythiophene, polyaniline, and poly(3,4-ethylenedioxythiophene), have been reported to be good candidates for electrochromic materials [37–38]. The possibility of preparing thin films of the $\text{Me}_2\text{N-T}_2\text{-NO}_2$ opens the possibility of exploring the occurrence of electrochromism in their films.

To study the electrochromism of cast and LB films, the in situ visible spectra of coated ITO transparent electrodes immersed in the electrolytic solution were recorded. The first reference spectrum was registered with the film immersed in the solution, in the absence of an external potential. Then, UV–vis spectra were taken

at controlled potential values. The electronic absorption spectra of a 20 layers LB assembly measured in situ at different voltages (step increment of 0.3 V) are shown in Fig. 11.

At open circuit, the spectra of LB and cast films immersed in KCl, also showed the Davydov splitting observed in air. However the polarity of water caused differences in the sharpness and the relative intensities of the peaks associated to H and J aggregates. When positive potentials of 0.3 and 0.6 V were applied, only small changes in the spectra were observed. At 0.9 V, the spectra of films of $\text{Me}_2\text{N-T}_2\text{-NO}_2$ showed two absorption bands: one intense band at 399 nm (with a shoulder at 550 nm) and a second band at 742 nm ascribable to the radical cation (oxidized form). The oxidation was reversible in LB films and in cast films and when the potential was biased to 0.0 V, the neutral form could be completely reproduced. The colour changes could be followed with the naked eye from violet to blue-greenish and vice versa.

The electrochromic behaviour of LB films and cast films was also tested under negative potentials. When a potential of -1.2 V was applied, a broad peak in the 450–600 nm region appear. In the case

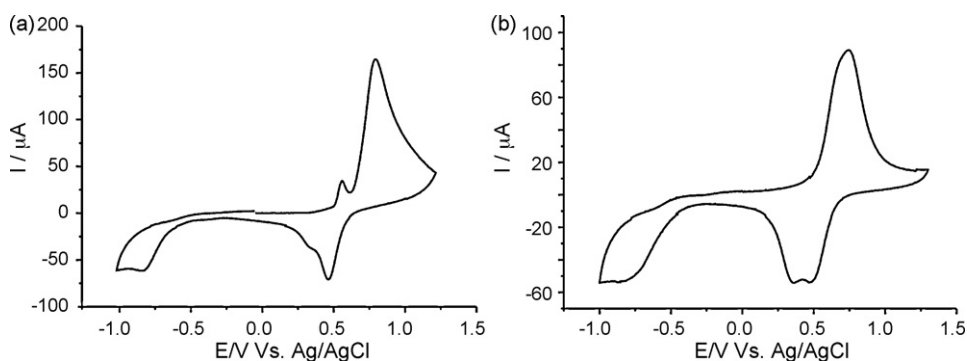


Fig. 10. Cyclic voltammograms of cast films of $\text{Me}_2\text{N-T}_2\text{-NO}_2$ deposited onto ITO glass and immersed in 0.1 mol L^{-1} KClO_4 . (a) First scan and (b) fifth scan.

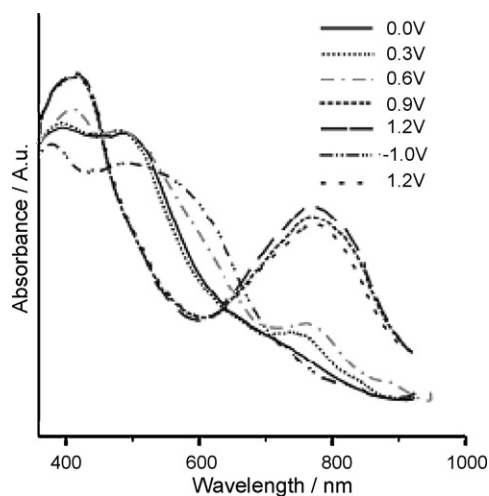


Fig. 11. Electronic absorption spectra of an LB film immersed in KCl 0.1 mol L⁻¹. Spectra registered in situ at different voltages.

of LB films, successive cycles allowed obtaining reproducible spectra. Only a small decrease of the intensity of the peak at 742 nm was observed. The reversibility was not complete in cast films and once the reduced form was obtained, it was not possible to recover the spectra of the neutral or the oxidized form.

The electrochromic behaviour of LB films was influenced by the nature of the anions solved in the electrolytic solution. When immersed in a solution containing an oxidant anion such as KClO₄, films changed their colour at lower potentials. This is consistent with the results shown in Figs. 9 and 10. The spectral and redox changes accompanying the applied voltage could be used to produce ionochromic and amperometric ion sensor electrodes. Chromatic (from violet to blue-greenish) and amperometric (0.7–0.9 V) changes are obtained in a few seconds.

4. Conclusions

The large dipolar moment of push-pull bithiophene Me₂N-T₂-NO₂ molecules, have led to Langmuir-Blodgett films and cast films with highly ordered supramolecular structures. UV-vis spectra of LB films and cast films showed characteristic splittings and shifts associated to strong intermolecular interactions that lead to high organisation. By comparing the FTIR spectra of KBr pellets and the Transmission and the RAIR spectra of LB and cast films, it was possible to determine that in both cases molecules are arranged perpendicularly to the surface. Spectroscopic and AFM results reveal certain differences exist in the organisation of both types of films.

The electrochemical and electrochromic properties of the films are influenced by the organisation of the molecules. The electrochromic films exhibited a colour change from violet to blue-greenish and vice versa on electrochemical oxidation and reduction. The modification of the intensity of the original violet colour could be followed visually. Thin films change their spectroelectrochemical properties when exposed to different ambiances. The spectral and redox changes accompanying the applied voltage could be used to produce ionochromic and amperometric ion sensor electrodes.

Although the spectroelectrochemical properties of films prepared using the LB technique and the casting technique are similar, LB films are preferred as sensor devices because the control on the structure is higher. The reversibility of the electrochemical sensing process was also improved in LB films.

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Biographies

María Luz Rodríguez-Méndez is Professor in the Department of Inorganic Chemistry at the University of Valladolid (Spain). She received the degree in Chemistry from the University Complutense of Madrid (Spain) in 1984 and the PhD. in chemistry from the University of Valladolid (Spain) in 1990. She has been working in the preparation and the structural characterisation of thin films of organic materials and their potential applications. Her main current interest is in the development of sen-

sors based on phthalocyanines and on conducting polymers. At the present moment she is involved in the development of an electronic nose, an electronic tongue and an electronic eye for the assessment of the organoleptic characteristics of wines and olive oils. She is author or co-author of over 90 publications.

Constantin Apetrei is a Senior Lecturer of the Department of Chemistry at the University “Dunărea de Jos” of Galați (Romania). He received his BSc in chemistry-physics (1997) from the University “Al. I. Cuza” Iasi and his PhD in chemistry (2007) from the University “Dunărea de Jos” of Galați. His current field of research interests includes development of chemically modified electrodes and their use in electronic tongues. He is author or co-author of over 20 publications.

Marina Nieto obtained her PhD from the University of Vigo (Spain). She was a Post Doc at the University of Valladolid and she is currently contracted at the Materials Science Institute of Madrid (ICMM-CSIC), Spain.

Víctor Hernández Jolín is a Professor (Aggregate Professor) at the Department of Physical Chemistry of the University of Málaga (Spain). He received his BSc in Chemistry (1987) and his PhD in Chemistry (1991) by the University of Málaga. He spent three years in a postdoc position at the Polytechnic of Milan (Italy), at the time that he was also a former student of the International School on Polymers Science “Giulio Natta”. In January 1995, he joined the academic staff of the University of Málaga. His main research activity is devoted to the study of polyconjugated organic polymers and oligomers, both in their neutral and doped states, by means vibrational and electronic molecular spectroscopies, electrochemistry, spectroelectrochemistry and quantum chemical computations. He has co-authored over 120 scientific articles, most of them in close cooperation with many foreign scientific teams, very active in this expanding field of research, and from several international laboratories and academic institutions.

Juan T. López Navarrete is a Full Professor of Physical Chemistry at the Universidad de Málaga (UMA). He received his BS degree from Universidad de Extremadura (1982) and a PhD in Chemistry from UMA in 1985. He worked as a postdoctoral fellow (1986–1988) at the Politecnico di Milano (Italy) with Prof. G. Zerbi on organic conducting polymers. His research interests include the application of Raman spectroscopy to π -conjugates systems, carbon nanostructures and electroactive molecules.

Franz Effenberger first studied with the aim of professional textile engineering at the Textile Engineering School in Krefeld, then chemistry at the Technische Hochschule Stuttgart. In 1959 in Stuttgart with an investigation of condensed heterocyclic ring systems doctorate. In 1971 he received a call to the Chair of Organic Chemistry at the Technical University of Stuttgart. He was from 1980 to 1986 Vice-rector of research at the University of Stuttgart, and significant contribution to the establishment of Bioprocessing involved. Franz Effenberger was rector of the University of Stuttgart from 1986 to 1990. In 1998 he was retired. The research priorities of Effenberger included the chemistry of aromatics, heterocycles and amino acids, the chemical foundations of molecular electronics and applications of enzymes in the synthesis. He has written over 300 original publications and 40 patents in these areas are published.

José Antonio de Saja is a Professor and Head of the Department of Condensed Matter Physics at the University of Valladolid. His present research interest is at the intersection of materials science, physics, physical chemistry and device engineering and focus on novel sensing materials. He is the head of the Group of Sensors at the University of Valladolid. At the present moment he is coordinating a UE Project devoted to the development of an electronic nose, an electronic tongue and an electronic eye for the assessment of the organoleptic characteristics of wines and olive oils. He is author or co-author of over 270 publications and has edited seven books.