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Comparative study of the electrosynthesis and characterization of films made from 1,1'-binaphthyl and 2-methoxynaphthalene

Received: 30 June 2004 / Revised: 4 August 2004 / Accepted: 6 September 2004 / Published online: 1 December 2004
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Abstract Oligomers of 2-methoxynaphthalene and 1,1'-binaphthyl were electrochemically synthesized by cyclic voltammetry (CV) in 0.1 M tetrabutylammonium hexafluorophosphate–nitrobenzene (TBAPF₆–NB). The redox characterization of the films was studied in monomer-free 0.1 M TBAPF₆–NB and 0.1 M tetrabutylammonium hexafluorophosphate–acetonitrile (TBAPF₆–ACN) solutions. The electrochemical response from the anodic charging (p-doping) of an oligo(1,1'-binaphthyl) film in both solvents consists of a continuously increasing current without a well-defined oxidation peak. Upon discharging the film a distinct reduction peak can be seen. The p-doping response of an oligo(2-methoxynaphthalene) film in both solvents consists of a prepeak followed by a plateau until the new electrochemical process starts. On the reverse scan two poorly resolved reduction peaks which merge into a broad cathodic peak as the scan rate increases can be observed. The cathodic charging and discharging (n-doping) response of 2-methoxynaphthalene film in 0.1 M TBAPF₆–ACN consists of a broad and well-defined redox peak. The structures of the film were studied by Raman and Fourier transform infrared spectroscopy (FTIR). Both techniques provide complementary vibrational information on the coupling of the starting materials studied. The morphologies of the electrosynthesized films were studied by scanning electron microscopy (SEM). The influence of the two substituents, the methoxy and naphthyl groups, on the

electrosynthesis properties of the naphthalene molecule was studied.

Introduction

Fused ring systems and ladder-type polymers have attracted a great deal of interest in the field of conducting polymers, from both theoretical and experimental viewpoints [1]. Monomers with fused ring structures give rise to films of network polymers, which can be both n- and p-doped. These materials have received considerable attention due to their promising electrical, electrochemical and optical properties that may find use in several applications, for example in semiconductor devices, light emitting electrochemical cells, energy storage, electrochromic devices, supercapacitors, solar cells and electrochemical sensors [2, 3].

Reports on the electrochemical synthesis and characterization of polymers based on naphthalene over the past 20 years have been rather sparse. Poly(*p*-phenylene) and polynaphthalene were prepared by nickel-catalyzed polycondensation of Grignard reagents from the corresponding dibromides by Sato et al [4]. Satoh et al studied the electropolymerization of naphthalene in a solution containing CuCl₂ and LiAsF₆ as the electrolyte [5, 6], and found similar results to those reported by Sato et al [4]. The properties of polynaphthalene films obtained from anodic coupling of naphthalene [7] and from cathodic coupling based on the nickel-catalyzed reduction of dibromoaromatics have been described by Zotti et al [8]. Poly(1,4-naphthalene) films obtained using a composite electrolyte of aluminum chloride and copper (I) chloride have been reported [9] as well as layered poly(naphthalene) films prepared by oxidation of naphthalene in BF₃-ethyl ether solution containing water [10]. Additionally, the redox potentials of α , α -binaphthyl and β , β '-binaphthyl have been studied by

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Heinze et al in $\text{SO}_2/0.1 \text{ M TBAPF}_6$ [11]. In a preliminary study, we reported the electropolymerization of 2-methoxynaphthalene in ACN-TBAPF_6 [12].

The influence of the side groups, methoxy and naphthyl, on the electrosynthesis of the naphthalene molecule in 2-methoxynaphthalene and 1,1'-binaphthyl monomers is studied in this work. We present a systematic study of the anodic electrosynthesis and the electrochemical, spectroscopic and morphological characterization of oligomeric films obtained from 1,1'-binaphthyl and 2-methoxynaphthalene in 0.1 M tetrabutylammonium hexafluorophosphate-nitrobenzene ($\text{TBAPF}_6\text{-NB}$).

Experimental

The electrochemical polymerization of oligo(2-methoxynaphthalene) and oligo(1,1'-binaphthyl) and the charging-discharging reactions of the films formed were carried out by potential cycling in a conventional three-electrode one-compartment cell at room temperature ($T=23 \text{ }^\circ\text{C}$). The cell was connected to an Autolab PGSTAT 100 potentiostat using general-purpose electrochemical system (GPES) software. A Pt disk (area: 0.07 cm^2) was used as the working electrode, and a Pt-wire wrapped around the glass body of the working electrode was used as the counter electrode. Ag/AgCl wire was used as a quasi-reference electrode and it was calibrated versus the ferrocene/ferrocinium couple. The redox potential of ferrocene $E_{\text{redox}} = (E_{\text{ox}} + E_{\text{red}})/2$ was $+0.35 \text{ V}$ versus this reference electrode. All the potential data reported in this work are, unless otherwise stated, given versus this reference electrode. The starting materials were 2-methoxynaphthalene (Acros) and 1,1'-binaphthyl (98% Acros), and both were used as received. Tetrabutylammonium hexafluorophosphate (TBAPF_6 , 99%, Fluka) in nitrobenzene (NB, Fluka) and acetonitrile (ACN, Lab-Scan) was used as the electrolyte salt in the polymerization and in the redox experiments. The concentration of the salt was 0.1 M in all the experiments. The salt was dried at $80 \text{ }^\circ\text{C}$ for 1 h under vacuum before use. Nitrobenzene was dried over basic alumina (Aldrich), and acetonitrile was stored over CaH_2 , freshly distilled and dried over basic alumina (Aldrich). All solutions were deaerated for 10 min with N_2 prior to measurement, and during the measurements a stream of N_2 was passed over the solutions.

Fourier transform infrared spectroscopy (FTIR) spectra were recorded from KBr pellets with a Bruker IFS66S FTIR instrument equipped with a MCT detector with resolution 4 cm^{-1} .

Raman spectra were recorded at room temperature on a Renishaw Ramascope (system 1000) equipped with a Leica DMLM microscope and connected to a CCD-camera as detector. The excitation wavelength for the Raman scattering was provided by a diode laser operating in the near IR range ($\lambda_{\text{ex}} = 780 \text{ nm}$) at low laser

power ($\leq 17 \text{ mW}$). Spectra were collected at 180° to the excitation beam.

The surfaces of the films formed were studied using scanning electron microscopy (SEM) with a Leica Cambridge LTD Stereoscan 360.

Results and discussion

Electrochemical polymerization

In the following section we report a comparative study on the polymerization of 0.05 M solutions of 1,1'-binaphthyl and 2-methoxynaphthalene in 0.1 M $\text{TBAPF}_6\text{-NB}$. Potential scanning was made between 0 and 1.8 V at scan rates of 20, 50, 100 mV s^{-1} . The cyclic voltammograms obtained at a scan rate of 20 mV s^{-1} during the polymerization of 1,1'-binaphthyl are shown in Fig. 1a. With every cycle an increase in current is observed at all scan rates, reflecting the growth of the film on the electrode surface. From the experimental

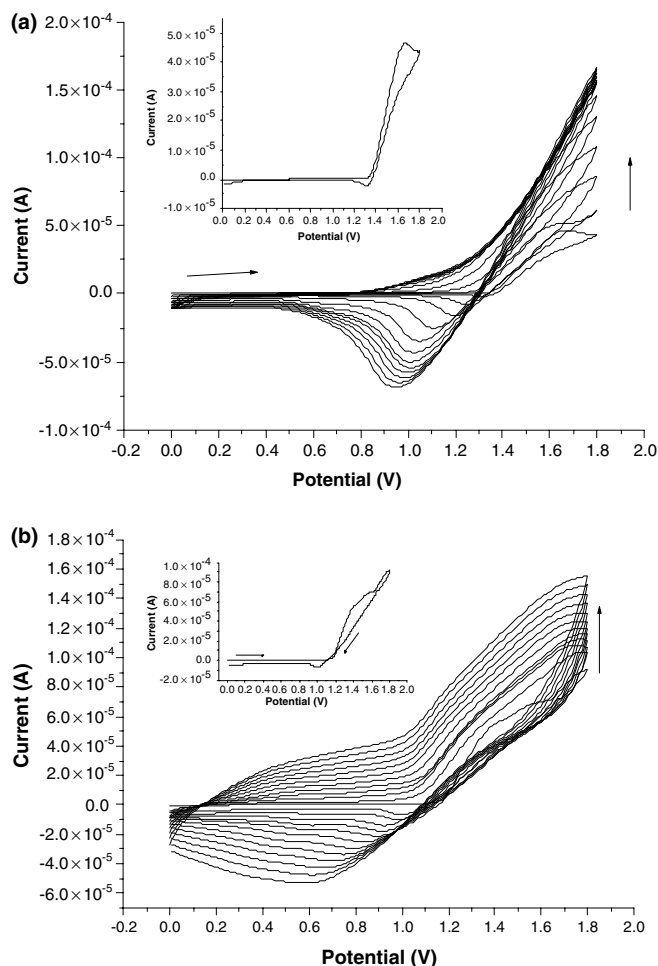


Fig. 1 Electrochemical polymerization by potential cycling between 0 and +1.8 V (12 cycles) on a Pt-disc electrode in 0.1 M $\text{TBAPF}_6\text{-NB}$ solution containing **a** 0.05 M 1,1'-binaphthyl at 20 mV s^{-1} and **b** 0.05 M of 2-methoxynaphthalene at 50 mV s^{-1}

results with different scan rates it was concluded that the best polymerization (in terms of the charging response of the film versus the charge used for polymerization) occurred at the scan rate of 20 mV s^{-1} . The first scan is shown in the insert in Fig. 1a. An oxidation peak at approximately 1.6 V can be seen during the two first scans due to the oxidation of the monomer species to the radical cation. Upon the reverse scan, a cathodic peak was visible at approximately 1.3 V due to the reduction of species produced during the forward scan. Upon consecutive scanning, only an increasing oxidation current is seen during the forward scan. In the reverse scan a well-defined reduction peak that displays increasing current as the number of scans increases can be observed.

In the case of 2-methoxynaphthalene, the influence of the scan rate on the film deposition was small. Film formation takes place at all scan rates used. Figure 1b shows the anodic oxidation of 2-methoxynaphthalene in 0.1 M TBAPF₆-NB at 50 mV s^{-1} . This scan rate was chosen for the production of films based on the response from the amount of active material adsorbed onto the electrode after polymerization. The first scan is shown in the insert in Fig. 1b. The crossover effect of the current is only observed during the first scan. Two different oxidation processes can be seen in the initial scan. The first wave is from the oxidation of 2-methoxynaphthalene leading to the radical cation, which is not stable under the experimental conditions. The second oxidation can be discerned at a more positive potential. This peak might be related to further oxidation of the radical cation, forming a dication, as reported for 9,10-diphenylanthracene [13]. If the forward scan is stopped at the potential between the two oxidation waves, no adsorption of material onto the electrode is observed.

During subsequent scans, the increasing oxidation current results in a merging of the peaks. The reduction peak is very broad and shifts to less positive potentials as the thickness of the film increases. A black film is deposited on the electrode surface.

The observed differences in film formation and its dependence on the scan rates between the two systems can be explained in terms of how the electronic natures and positions of the substituents affect the kinetics and the type of coupling processes in the follow-up reactions [14]. In 1,1'-binaphthyl, the torsion angles between the two naphthalene units are very high (48°) leading to a small π -overlap [15]. Steric factors can therefore influence the kinetics of the coupling reaction. In addition, the solubility of the monomer in nitrobenzene is rather low. These factors are responsible for the observation that 1,1'-binaphthyl undergoes slower reactions. This conclusion is based on the experiments showing the dependence of the scan rate on the yield of adsorbed material. The slower the scan rate, the more visible the electrode coating and the larger the oxidation current.

The methoxy group at position two in 2-methoxynaphthalene facilitates oxidation due to the presence of the free electrons on the oxygen atom in the methoxy

group, and it stabilizes the radical cation. The methoxy group, on the other hand, minimizes the coulombic repulsion between the charged species formed, enhancing the rate of the coupling process [14]. Despite the fact that the methoxy group has a great influence on the oligomerization reaction, it is not clear whether the coupling rate of the oxidized species or the diffusion of them to the bulk of the solution is the dominant process. Therefore 50 mV s^{-1} might be the scan rate when the balancing of both processes is achieved with more accuracy, and when a material with less defects and a higher conjugation length is obtained.

Electrochemical studies by Heinze et al [16] on a series of substituted thiophenes have shown that methoxy groups substituted at the “ β ” position on terminal rings give stable cation radicals. This stability is greater than that of other small oligomers lacking the $-\text{OCH}_3$ group.

The oligomerization of 2-methoxynaphthalene has previously been studied by us in 0.1 M tetrabutylammonium hexafluorophosphate-acetonitrile (TBAPF₆-ACN) [12]. Films obtained in this work in 0.1 M TBAPF₆-NB are thicker and have higher charging capacities than films obtained in 0.1 M TBAPF₆-ACN. It is well known that both the physical and chemical properties of the solvent have a great influence on the oligomerization reaction [13]. Radical cations of aromatic hydrocarbons are sensitive to nucleophilic attack in the solvent-electrolyte system. They can react more easily with acetonitrile, which has a higher donor number (DN=14.1) than with nitrobenzene (DN=4.4) and so they undergo undesirable follow-up reactions with the solvent.

Redox characterization

Figure 2 shows cyclic voltammograms for the electro-synthesized 1,1'-binaphthyl film with different switching potentials at 20 mV s^{-1} scan rate in 0.1 M TBAPF₆-NB. From the results it is obvious that at a switching potential of 1.2 V the system does not give a good p-doping response. A poorly defined anodic peak can initially be seen at potentials higher than 1.4 V. The current increases with increasing switching potentials. A broad cathodic peak on the reverse scans can clearly be seen. It is also worth pointing out that no degradation processes took place even though the film was cycled up to 1.7 V. Based on the doping response of the system, increasing oxidation current with increasing switching potential without well-defined peaks, we may conclude that the film consists of oligomeric species probably containing oligomers of different lengths with different redox potentials that give rise to multiple overlapping peaks.

Figure 3a, b show cyclic voltammograms of an electro-synthesized film of 2-methoxynaphthalene between -0.5 and 1.4 V in 0.1 M TBAPF₆-NB at scan rates of 20 and 50 mV s^{-1} respectively. At the lower scan rate a better resolved prepeak at approximately 0.55 V can be

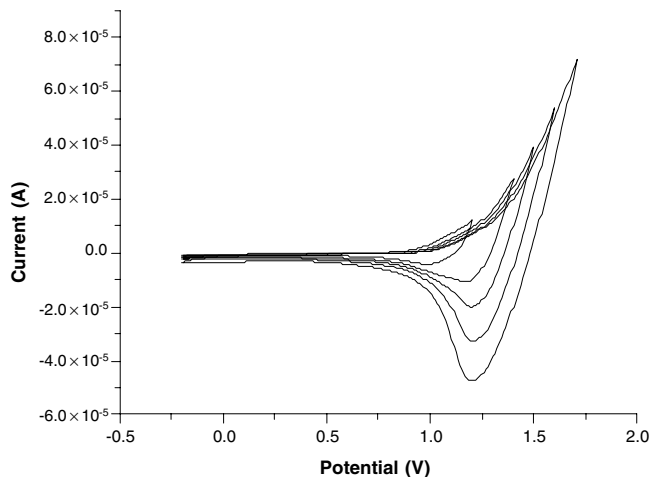


Fig. 2 Cyclic voltammogram of the 1,1'-binaphthyl film in 0.1 M TBAPF₆-NB (p-doping) at a scan rate of 20 mV s⁻¹. The film was made by potential cycling between 0 and +1.8 V on a Pt-disc electrode (12 scans) in 0.1 M TBAPF₆-NB solution containing 0.05 M of monomer at a scan rate of 20 mV s⁻¹

seen. This peak shifts to more positive potentials as the scan rate increases, and a second anodic process starts at potentials above 1.4 V. On the reverse scan, two poorly-resolved reduction peaks are seen at approximately 1.1 and 0.4 V, whereas at a higher scan rate only a broad cathodic peak is observed. A possible explanation for the observed behavior is that during polymerization/oligomerization reactions defects are induced in the film, resulting in a conductive material that consists of oligomers of different effective conjugation lengths and consequently of redox states with different oxidation potentials. This explanation is supported by the following experimental results. When the p-doping response of the film electro synthesized at 20 mV s⁻¹ scan rate was compared with the film electro synthesized at 50 mV s⁻¹, it was observed that the prepeak was shifted to more positive potentials. This indicates that material with more defects, resulting in a lower conjugation length, was synthesized at 20 mV s⁻¹ than at 50 mV s⁻¹ scan rate. The slower the scan rate, the longer time the film is exposed to high positive potentials, and therefore there is a higher probability of follow-up reactions leading to structural defects. When the electro synthesized film made at 100 mV s⁻¹ was p-doped, the prepeak was shifted to less positive potentials. This is in agreement with the assumption that a material with less defects and a high effective conjugation length was formed at higher scan rates.

The film could be cycled up to 1.8 V without showing any evidence of degradation. The film is not completely discharged until potentials of -0.5 V are reached. From the experimental results we can conclude that in the case of 2-methoxynaphthalene we may have synthesized a network or cross-linked material (Fig. 3). This can be concluded from the broad charging response within the same potential range in comparison to 1,1'-binaphthyl films (Fig. 2).

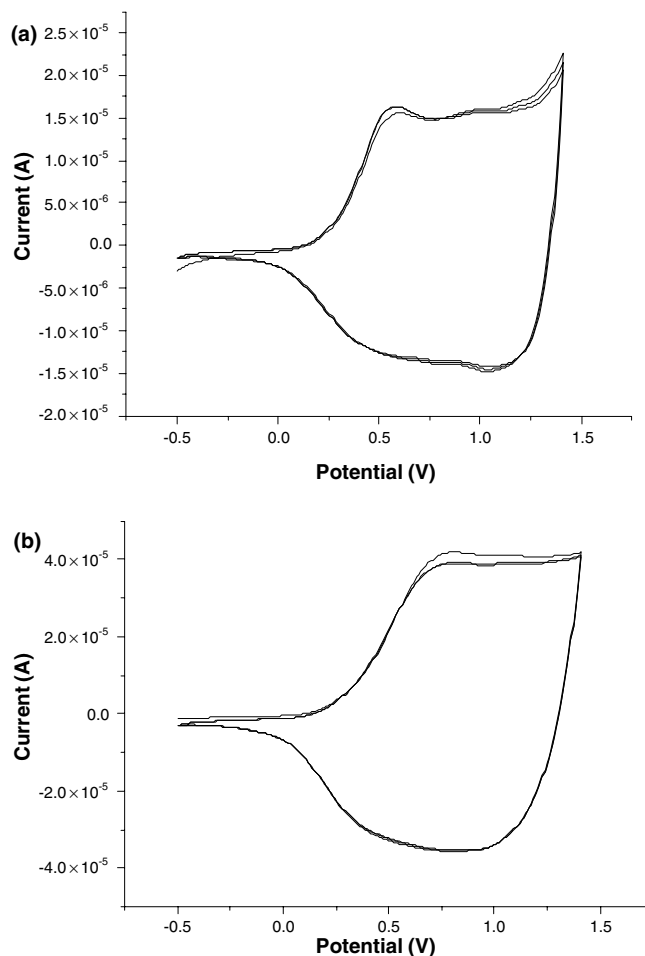


Fig. 3 Cyclic voltammogram of the 2-methoxynaphthalene film between 0 and 1.4 V in 0.1 M TBAPF₆-NB (p-doping) at a scan rate of **a** 20 mV s⁻¹ and **b** 50 mV s⁻¹. The film was made by potential cycling between 0 and 1.8 V on a Pt-disc electrode (12 scans) in 0.1 M TBAPF₆-NB solution containing 0.05 M monomer at a scan rate of 50 mV s⁻¹

The p-doping responses of 1,1'-binaphthyl and 2-methoxynaphthalene films electro synthesized in 0.1 M TBAPF₆-NB were also studied in 0.1 M TBAPF₆-ACN.

1,1'-Binaphthyl film was cycled starting from 0 V to increasing switching potentials between 1.2 and 1.6 V at 20 and 50 mV s⁻¹ scan rates (not shown here). Approximately the same results were observed as for p-doping in 0.1 M TBAPF₆-NB.

The cyclic voltammogram of the 2-methoxynaphthalene film in 0.1 M TBAPF₆-ACN (not shown here) is rather similar to that obtained in 0.1 M TBAPF₆-NB. The starting potential was 0 V and the switching potential was increased by 0.1 V from 1.0 to 1.5 V and scan rates of 20 and 50 mV s⁻¹ were used. The film was found to exhibit the best p-doping process when the switching potential was 1.2 V. At higher values, a decrease in the current response was observed, indicating that some degradation had taken place.

For both oligomeric systems it was observed that the film stability in 0.1 M TBAPF₆-ACN is less than in

0.1 M TBAPF₆-NB. A decrease in the current response in ACN indicates that some degradation of both films takes place at lower switching potentials in 0.1 M TBAPF₆-ACN than in 0.1 M TBAPF₆-NB. This can be explained in terms of differences in nucleophilicity between the solvents. ACN is more nucleophilic than NB and can react more easily with the film, leading to side-reactions.

Figure 4 shows a comparison between the n-doping responses of a 2-methoxynaphthalene film electro-synthesized in 0.1 M TBAPF₆-ACN (shown in a preliminary study) [12] and in 0.1 M TBAPF₆-NB during n-doping between 0 and -2.4 V at 50 mV s⁻¹ in 0.1 M TBAPF₆-ACN. The redox responses of both films electro-synthesized in different solvents are very different. We have reported in a previous work [12] that the 2-methoxynaphthalene film electro-synthesized in 0.1 M TBAPF₆-ACN shows well-defined multi-redox peaks during n-doping, which may originate from macromolecules of 2-methoxynaphthalene of different sizes in the resultant film. However, films resulting from the anodic oxidation of 2-methoxynaphthalene in 0.1 M NB-TBAPF₆ have a broad and well-defined cathodic peak at -1.5 V and the corresponding oxidation peak at -1.3 V. The voltammogram of 2-methoxynaphthalene film electro-synthesized in 0.1 M TBAPF₆-ACN is more characteristic of a macromolecular system, while the voltammogram of 2-methoxynaphthalene film electro-synthesized in 0.1 M TBAPF₆-NB is characteristic of oligomers with longer chain lengths. This later statement can be explained by the fact that, with increasing chain length, the potential difference between adjacent redox states decreases and they merge into a broad peak. In addition, the discharging peak potentials appear at lower energy in the film made from NB in comparison to the film made in ACN [17]. Furthermore, all of these features can be seen in the voltammograms of 2-meth-

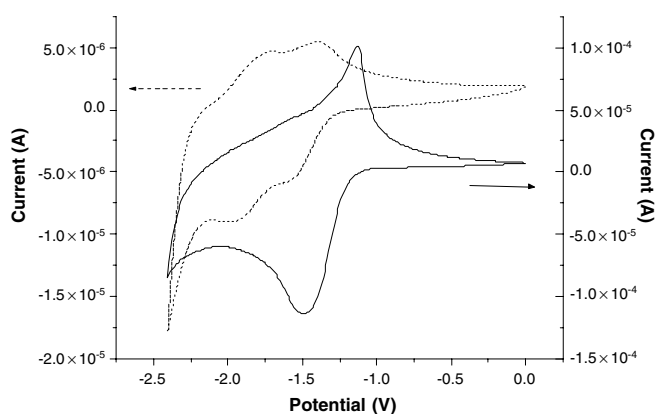


Fig. 4 Cyclic voltammogram of the 2-methoxynaphthalene film between 0 and -2.4 V in 0.1 M TBAPF₆-ACN (n-doping) at a scan rate of 50 mV s⁻¹. The film was made by potential cycling on a Pt-disc electrode (12 scans) (*broken line*) between 0 and +1.5 V in 0.1 M TBAPF₆-ACN, and (*continuous line*) between 0 and +1.8 V in 0.1 M NB-TBAPF₆ solution containing 0.05 M of monomer, at a scan rate of 50 mV s⁻¹.

oxynaphthalene film electro-synthesized in 0.1 M TBAPF₆-NB.

FTIR and Raman characterization

Raman and IR spectroscopies are vibrational techniques and provide complementary vibrational information. In FTIR spectroscopy, aromatic compounds give the strongest absorptions bands in the region 900–650 cm⁻¹ and these are due to C–H vibrations out of the plane of the aromatic ring. These bands are generally weak in Raman spectroscopy, where skeletal vibrations bands are strong. Therefore, Raman spectroscopy gives relevant information on the vibrations in the polymer chain backbone, and it is a technique commonly used to study carbon-based materials. [18, 19].

1,1'-Binaphthyl films were electro-synthesized in 0.1 M TBAPF₆-NB and 0.1 M TBABF₄-NB. The films were then soaked in fresh ACN in order to remove the remaining electrolyte salt and the solvent used in electro-synthesis. The FTIR transmission spectra of both electro-synthesized materials were then recorded as KBr pellets and are shown in Fig. 5. The insert in the Fig. 5 shows the spectrum of the monomer. It can be seen from the spectra that vibrations from the two films synthesized in different electrolytes are rather similar. This is an indication that the electrolyte salt has no effect on the material formed. No characteristic bands for the anions, 1060 cm⁻¹ for BF₄⁻ and 810 cm⁻¹ in the case of PF₆⁻, as well as for pure NB can be seen due to the efficiency of the soaking process.

The FTIR transmission spectra of a 1,1'-binaphthyl film electro-synthesized in 0.1 M TBAPF₆-NB (a) and the monomer (b) are shown in Fig. 6. Only the 1000–

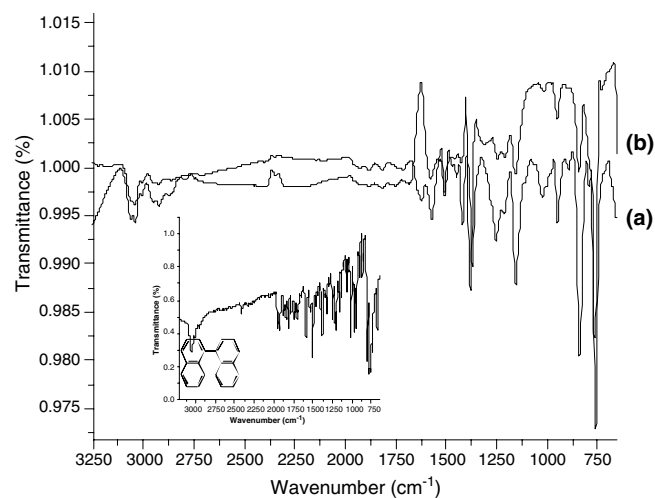


Fig. 5 FTIR transmission spectra of the 1,1'-binaphthyl films in KBr pellets. The films are made by potential cycling between 0 and +1.8 V on a Pt-disc electrode at a scan rate of 20 mV s⁻¹. **a** Film made in 0.1 M TBAPF₆-NB, and **b** TBABF₄-NB solution containing 0.05 M of 1,1'-binaphthyl. The insert shows an FTIR transmission spectrum for the monomer

600 cm^{-1} part of the spectrum is shown. The most significant vibrations take place in this range due to the out-of-plane C–H vibrations from the aromatic rings. The monomer gives its characteristic bands in the regions 800–775 and 780–760 cm^{-1} , where the out-of-plane C–H bending of three and four adjacent hydrogen atoms takes place, respectively. In addition, the spectrum of the monomer has a peak at 618 cm^{-1} , which can be assigned to the ring stretching of monosubstituted naphthalenes. However, in the spectrum of the film the number of strong IR modes decreases in comparison to the spectrum of the monomer. Furthermore, the spectrum of the electrosynthesized film has some characteristic bands at 760 and 839 cm^{-1} which can also be found in the spectra of phenylene oligomers [20] and poly(1,4-disubstituted naphthalene rings [7, 9, 10].

The FTIR transmission spectra of (a) 2-methoxynaphthalene film synthesized in 0.1 M TBAPF₆-NB and (b) 2-methoxynaphthalene film synthesized in 0.1 M TBABF₄-NB are shown in Fig. 7. The spectrum of the monomer is shown in the insert Fig. 7. Both films were soaked in fresh ACN after synthesis in order to remove the solvent (NB) and the electrolyte salt. No distinguishing spectral differences can be seen between the films, indicating that in this case the two electrolyte salts do not have any significant effect on the structure of the material formed. Furthermore, no characteristic bands for the electrolyte are seen. All of the vibrations present in the spectra originate from the film. In the region between 3000 and 1000 cm^{-1} , only small changes are observed between the spectra of the monomer and the electrosynthesized films. In this region, bands related to the methoxy group can be found at around 1460, 1395, 1260, and 1170 cm^{-1} , indicating that oligomerization does not affect the methoxy group.

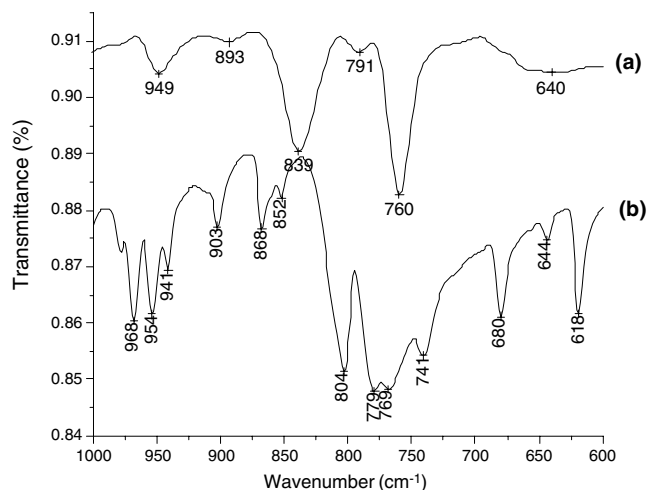


Fig. 6 a FTIR transmission spectra of the 1,1'-binaphthyl film and of the b 1,1'-binaphthyl monomer as KBr pellets. The film was made by potential cycling between 0 and +1.8 V on a Pt-disc electrode in 0.1 M TBAPF₆-NB solution containing 0.05 M of monomer at a scan rate of 20 mV s^{-1}

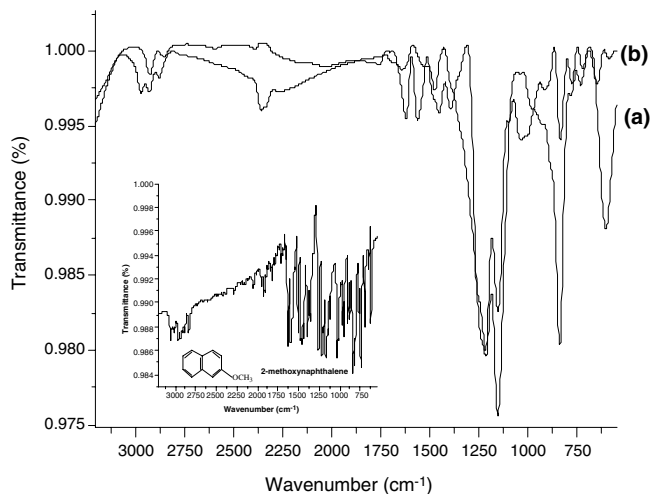


Fig. 7 FTIR transmission spectra of the 2-methoxynaphthalene films in KBr pellets. The films are made by potential cycling between 0 and +1.8 V on a Pt-disc electrode at a scan rate of 50 mV s^{-1} . a film made in 0.1 M TBAPF₆-NB, and b TBABF₄-NB solution containing 0.05 M of 1,1'-binaphthyl. The insert shows a FTIR transmission spectrum for the monomer

Figure 8 shows the spectra in the range of 1000–500 cm^{-1} of (a) the 2-methoxynaphthalene monomer and (b) the film synthesized in 0.1 M TBAPF₆-NB. The most important changes, frequently correlated with the substitution pattern, are observed in this wavenumber range. The monomer shows strong bands at 897, 874, 838, and 816 cm^{-1} , which may originate from the out-of-plane C–H bending of an isolated hydrogen atom and two adjacent hydrogen atoms in one ring. The bands at around 760–735 cm^{-1} are from four adjacent hydrogen atoms on the other ring. In the latter case two bands are

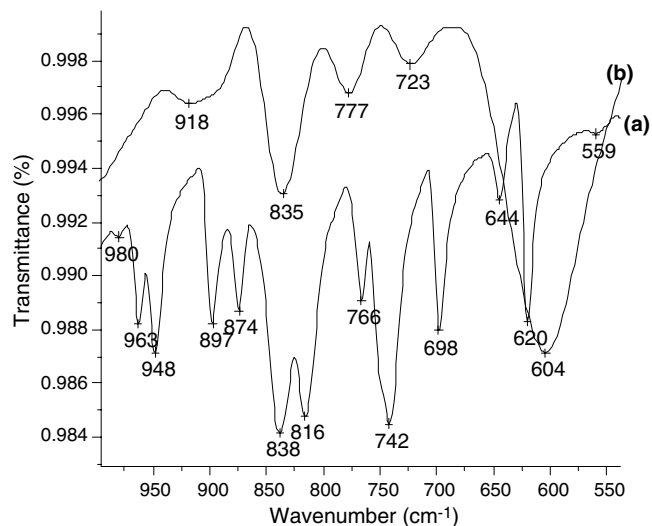


Fig. 8 a FTIR transmission spectra of the 2-methoxynaphthalene film and of the b 2-methoxynaphthalene monomer as KBr pellets. The film was made by potential cycling between 0 and +1.8 V on a Pt-disc electrode in 0.1 M TBAPF₆-NB solution containing 0.05 M of monomer at a scan rate of 50 mV s^{-1}

usually seen, but not always with the same intensity. The strong band at 620 cm^{-1} originates from stretching of monosubstituted naphthalene rings. However, the spectrum of the film shows fewer IR-active modes. The bands originating from the out-of-plane vibrations are greatly modified and the band at 620 cm^{-1} disappears. Furthermore, the band due to the out-of-plane vibration of one hydrogen is absent in the spectrum of the film. The spectrum of the film exhibits a strong peak at around 835 cm^{-1} . This band can be correlated to para substitution from the vibration of ortho-ortho phenyl rings but could also be assigned to the out-of-plane vibrations of isolated hydrogen atoms in substituted naphthalenes. The band at around 777 cm^{-1} may originate from out-of-plane vibrations of four adjacent hydrogen atoms in one ring. FTIR results indicate that a coupling of the aromatic rings, forming a larger conjugated system, may have taken place with both *o*- and *p*-substitution to the methoxy group, leaving one isolated hydrogen in one ring and four adjacent hydrogens on the other ring. In addition to the latter statement, it has been reported by other groups [7, 9, 10] that bands at around 760 and 840 cm^{-1} can be related to out-of-plane vibrations of a 1,4-disubstituted naphthalene ring.

The Raman spectra of the 1,1'-binaphthyl film in the neutral state after electro-synthesis in $0.1\text{ M TBAPF}_6\text{-NB}$, and the same film after p-doping in $0.1\text{ M TBAPF}_6\text{-ACN}$, are shown together with the spectrum of the monomer 1,1'-binaphthyl in Fig. 9. It can be seen that the spectrum of the film consists of fewer bands than the spectrum of the monomer. The bands in the film are also broader and shifted to lower wavenumbers,

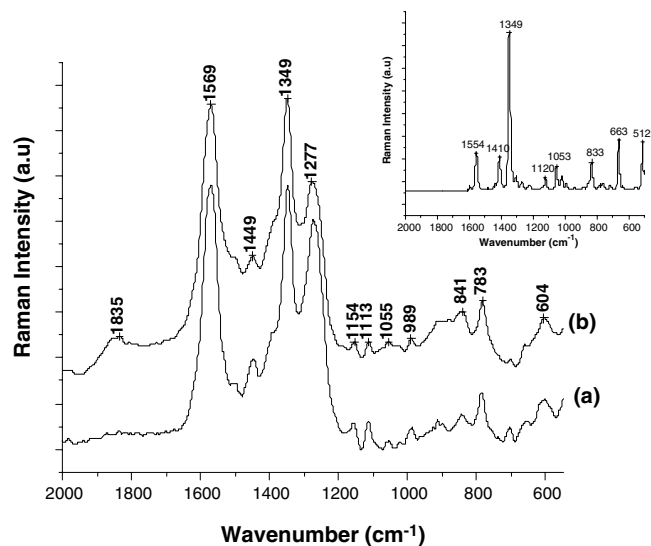


Fig. 9 Raman spectra ($\lambda_L = 780\text{ nm}$) of **a** electrochemically polymerized 1,1'-binaphthyl film in the neutral state on a Pt electrode, **b** the same film but after p-doping in $0.1\text{ M TBAPF}_6\text{-ACN}$. The insert shows the Raman spectrum of the monomer, 1,1'-binaphthyl. The 1,1'-binaphthyl film was polymerized in a 0.05 M solution of monomer in $0.1\text{ M TBAPF}_6\text{-NB}$ by potential scanning from 0 to $+1.8\text{ V}$ with a scan rate of 20 mV s^{-1}

which indicates an increase in the conjugation length. The Raman spectrum of the conjugated film is dominated by a few significant vibrations originating from the polymer backbone. The strongest modes are from aromatic C=C stretching: peaks at 1569 , 1449 , and 1349 cm^{-1} , and from inter-ring C-C stretching at 1277 cm^{-1} . The band at 1349 cm^{-1} can originate from either ACN or NB, since both solvents have characteristic bands around this wavenumber. However, 1,1'-binaphthyl monomer has a sharp and strong band at about 1349 cm^{-1} related to C=C stretching in mononaphthyl. This mode can even be seen in the spectrum of the film. Therefore, the band at 1349 cm^{-1} in the spectrum of the film may originate either from traces of the solvents ACN and NB left in the film, or from the polymer backbone itself.

Figure 10 shows the Raman spectra of the 2-methoxynaphthalene film in the neutral state after electro-synthesis in $0.1\text{ M TBAPF}_6\text{-NB}$, and the same film again in the neutral state after p-doping in $0.1\text{ M TBAPF}_6\text{-ACN}$. No structural differences can be seen between these films, indicating that the two different solvents used during p-doping do not have any significant effect on the material formed. The spectrum of the 2-methoxynaphthalene monomer is also included in the figure. Compared to the spectrum of the monomer, some changes in the spectrum of the film can be seen. These changes can be related to the formation of a polyconjugated material.

Raman spectra of electro-synthesized films of 2-methoxynaphthalene and 1,1'-binaphthyl both com-

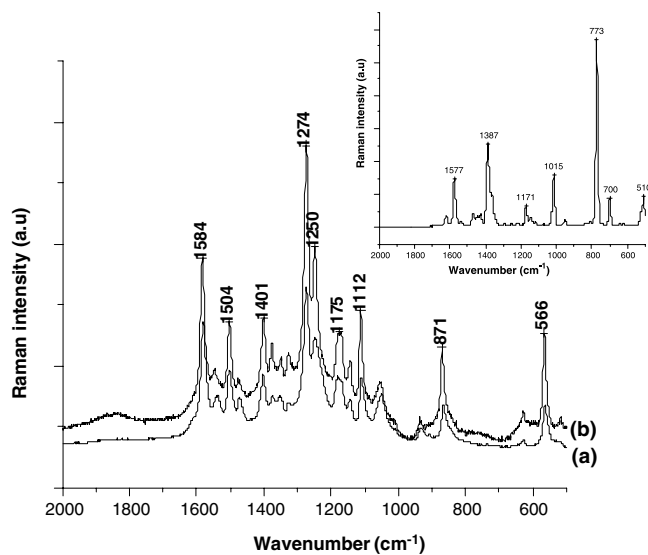


Fig. 10 Raman spectra ($\lambda_L = 780\text{ nm}$) of **a** electrochemically polymerized 2-methoxynaphthalene film in the neutral state on a Pt electrode, and **b** the same film but after p-doping in $0.1\text{ M TBAPF}_6\text{-ACN}$. The insert shows the Raman spectrum of the monomer, 2-methoxynaphthalene. The 2-methoxynaphthalene film was polymerized in a 0.05 M solution of monomer in $0.1\text{ M TBAPF}_6\text{-NB}$ by potential scanning from 0 to $+1.8\text{ V}$ with scan rate of 50 mV s^{-1}

monly show a band near 1600 cm^{-1} and two bands between 1300 and 1200 cm^{-1} . In the spectrum of the 2-methoxynaphthalene film these bands are narrower than in the spectrum of 1,1'-binaphthyl film and they are shifted to lower wavenumbers. A possible explanation for these experimentally-found phenomena might be, on the one hand, an increase in the conjugation length in the 2-methoxynaphthalene case, indicating large π electron delocalization, and on the other hand the influence of the methoxy group on the vibrational behavior of the film. Moreover, the $-\text{OCH}_3$ group has some characteristic bands in the range $1270\text{--}1060\text{ cm}^{-1}$. These bands can be associated with the C–O–C asymmetric stretching vibration. In the monomer spectrum, these vibrations can be seen at 1015 cm^{-1} , and in the film spectra at 1051 cm^{-1} . A possible explanation of the shift of this band is that, as a result of resonance, aromatic ethers have a contribution from $=\text{O}^+$ which tends to increase the force constant of the C–O bond of the aromatic rings and therefore increases the C–O stretching vibration frequency.

Finally, it is worth pointing out that the spectra of the electrosynthesized films in $0.1\text{ M TBAPF}_6\text{-NB}$ in the neutral electronic state and the same film after p-doping in $0.1\text{ M TBAPF}_6\text{-ACN}$ show the same characteristic bands, and the relative intensities of the bands in both spectra remain almost unchanged. The fact that the change of solvent does not affect the film structure is of great interest for further applications.

The Raman spectrum of the 1,1'-binaphthyl film, and to certain extent the spectrum of 2-methoxynaphthalene film, show some similarities with the spectrum of disordered graphite, which has two Raman peaks at 1580 and 1330 cm^{-1} . These peaks can be correlated to the so-called G and D bands of disordered graphite, respectively. Materials containing small islands of condensed aromatic rings have the same features, probably due "to the aromatic structure of graphite matrix" [21, 22].

Morphology: SEM characterization

The film morphology was analyzed by SEM. SEM pictures showing the surface of the dry 1,1'-binaphthyl film electropolymerized in 0.05 M of 1,1'-binaphthyl in $0.1\text{ M TBAPF}_6\text{-NB}$, and the same film in the dry neutral state but after p-doping in $0.1\text{ M TBAPF}_6\text{-ACN}$, are shown in Fig. 11a, b, respectively. As can be seen in Fig. 11a, the electropolymerized film shows a porous structure, and even after p-doping (Fig. 11b) the film still has the same porous structure.

Figure 12a shows a SEM picture of the surface of a dry 2-methoxynaphthalene film electropolymerized in $0.1\text{ M TBAPF}_6\text{-NB}$ and then reduced to the neutral electronic state. Here the film consists of a cloudy structure. However, the SEM picture of the same film after p-doping in $0.1\text{ M TBAPF}_6\text{-ACN}$ (Fig. 12b) shows a much smoother structure. A possible explanation might be that the morphology of the film is some-

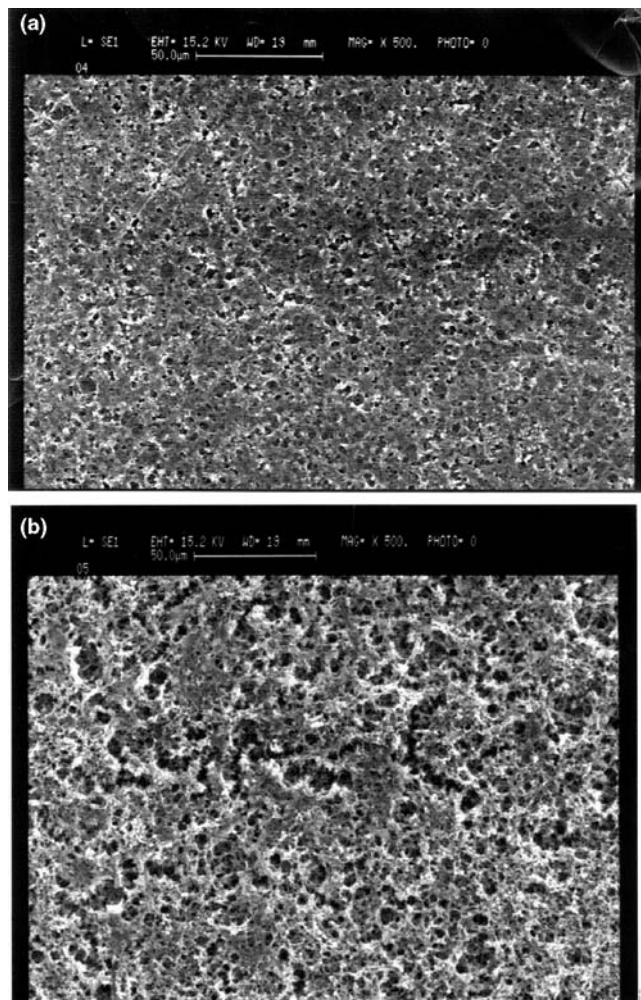


Fig. 11 Scanning electron micrographs of the surface of the 1,1'-binaphthyl film electrode. Magnification $\times 500$. **a** Image of a freshly-made film in $0.1\text{ M TBAPF}_6\text{-NB}$; **b** the film after p-doping in $0.1\text{ M TBAPF}_6\text{-ACN}$

how affected by the change in solvent. It is interesting to note that although changes in the morphology of the film took place in this process, the Raman spectrum of the film did not change; see Fig. 10.

It can be further stated that the entire surface of the Pt electrode was covered with both films, but we estimated visually that the 1,1'-binaphthyl films were thicker than the films electrosynthesized from 2-methoxynaphthalene.

Conclusions

Reproducible and stable films were obtained by anodic coupling of 1,1'-binaphthyl and 2-methoxynaphthalene in $0.1\text{ M TBAPF}_6\text{-NB}$.

The redox responses of the two systems, however, were very different. Earlier work had shown how redox potentials are markedly dependent on the chain length as well as on the structure [23]. Electrosynthesized 2-

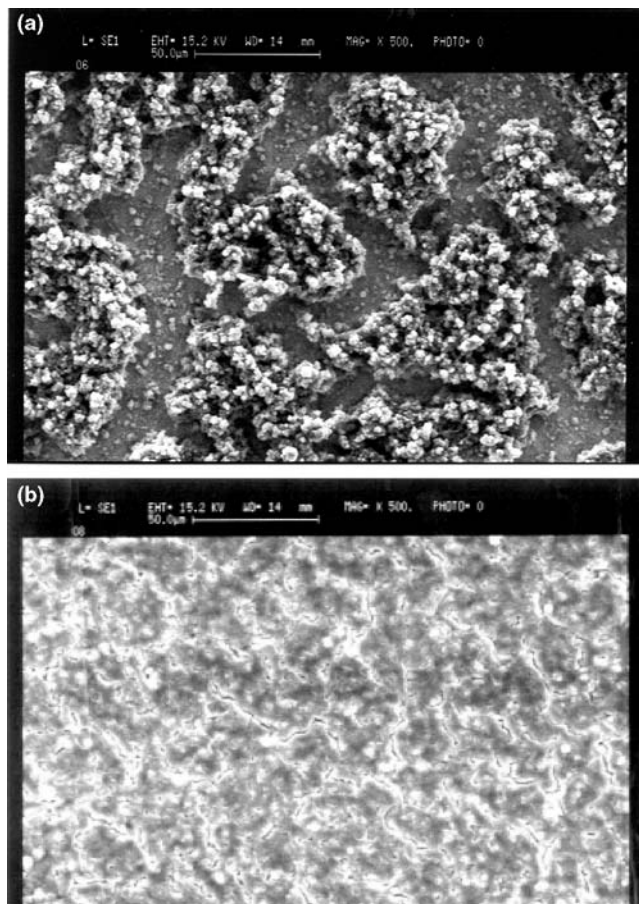


Fig. 12 Scanning electron micrographs of the surface of the 2-methoxynaphthalene film electrode. Magnification $\times 500$. **a** Image of a freshly-made film in 0.1 M TBAPF₆-NB; **b** the film after p-doping in 0.1 M TBAPF₆-ACN

methoxynaphthalene film has a lower oxidation potential due to a better stabilization of the inserted charges due to a higher degree of conjugation length in the film. In addition, the methoxy group in the film structure lowers the oxidation potential, just as it does in the monomer. The 2-methoxynaphthalene film can also be charged to a higher level in the doping process. This results in considerable energetic gaps between adjacent energy states in the material, which can be seen as different redox processes in the voltammograms. The broad and well-defined redox peaks in the n-doping of 2-methoxynaphthalene film indicates an oligomeric structure. On the other hand, the redox behavior of electrosynthesized 1,1'-binaphthyl film shows quite undefined p-doping, and an absence of hysteresis, which is characteristic of oligomeric species with shorter chain lengths in comparison to films obtained from 2-methoxynaphthalene synthesized in 0.1 M TBAPF₆-NB.

Spectroscopic results confirm the formation of conjugated materials with both monomers. Characteristic

IR vibrations for poly 1,4-disubstituted naphthalenes were found in the spectra of both electrosynthesized films. Raman spectra of 1,1'-binaphthyl films and 2-methoxynaphthalene films show some characteristic bands of disordered graphite.

The SEM results show that electropolymerized films from 1,1'-binaphthyl and 2-methoxynaphthalene have quite different morphologies, which may partly explain the differences observed in their redox responses.

Acknowledgements Financial support from the Graduate School of Materials Research is gratefully acknowledged (BME). This work forms part of the activities being pursued at the Åbo Akademi Process Chemistry Centre, within the Finnish Centre of Excellence Programme (2000–2005) of the Academy of Finland. Mr. C. Ekholm is gratefully acknowledged for the SEM pictures of the electrode surfaces.

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