

# Synthesis and electropolymerisation of pyrrol-1-yl substituted phthalocyanines

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2,9,16,23-Tetrakis(2-pyrrol-1-ylalkoxy)phthalocyanines, in which the phthalocyanine is connected *via* an alkylene spacer to a pyrrole substituent, are prepared *via* three steps in good yields. For the first time monomers with groups for electropolymerisation electronically isolated from the phthalocyanine are described. Films of thickness up to 5  $\mu\text{m}$  of these pyrrole substituted phthalocyanines were obtained by oxidative electropolymerisation under potentiodynamic conditions or at constant potential. UV/Vis spectra show the presence of phthalocyanine and polypyrrole structural units in the polymers. The charge–discharge behaviour is accompanied by a reversible electrochromic colour change. The polymer films exhibit specific electrical conductivities of  $\sim 10^{-5} \text{ S cm}^{-1}$ .

## Introduction

The most common methods for the preparation of thin films of low molecular weight phthalocyanines on suitable carriers are physical vapor depositions,<sup>1,2</sup> the Langmuir–Blodgett-technique,<sup>3</sup> simple coating processes<sup>4</sup> or micellar disruption processes.<sup>5</sup> These films are, for example, interesting as photoconductors,<sup>6</sup> photovoltaic devices,<sup>2</sup> in photoelectrochemical cells,<sup>2</sup> organic field effect transistors<sup>7</sup> or electrochromic films.<sup>8</sup> Polymeric phthalocyanine networks, on the other hand, are attractive materials because of their rigidity, high stability and strong, well-defined coupling of the electronic  $\pi$ -systems. Because polymeric phthalocyanines are not soluble and cannot be vaporized, however, new methods of thin film formation were developed for these materials. By reaction of gaseous tetracarbonitriles like 1,2,4,5-tetracyanobenzene with metal surfaces thin films of the polymers were obtained.<sup>8,9</sup> More recently, the electropolymerisation of suitable substituted porphyrins<sup>10</sup> and phthalocyanines<sup>11</sup> was used for the formation of thin films of polymers of these macrocyclic compounds. In this case the monomers for electropolymerisation are substituted *i.e.* by amino, pyrrole or thiophene groups.

Electropolymerisation has the advantage that a wide variety of conducting surfaces (metals, conducting metal oxides, carbon-based electrodes) can be used, and that the film thickness can be directly controlled by the polymerisation conditions, the scan rate, potential range, polymerisation time and type of the electrolyte. Several papers describe the oxidative electropolymerisation of 2,9,16,23-tetraaminophthalocyanine<sup>11–17</sup> and in one case of 2,3,9,10,16,17,23,24-octacyanophthalocyanine.<sup>11,18</sup> The electrocatalytic and sensoric properties in several reactions<sup>11,19,20</sup> and the electrochromism were investigated.<sup>11</sup>

In the phthalocyanines described so far the group for electropolymerisation such as an aromatic amino group is directly connected to the macrocyclic ring system thus leading to polymers in which the phthalocyanine electronic system is included in the conjugated system. This influences the optical

and electronic properties of the thin films produced. In addition, the direct connection of the polymerisable group to the rigid phthalocyanine may lead to steric hindrance during the polymerisation reaction resulting in low conversion and low average molecular weight. Investigations of pyrrole-substituted porphyrins showed that monomers with separated electropolymerisable groups were extremely suitable for oxidative electropolymerisation.<sup>10,21,22</sup> In this paper a phthalocyanine with a polymerisable group which is separated by an electronically insulating alkylene spacer from the phthalocyanine macrocycle is described, to our knowledge for the first time, to separate efficiently the conjugated polymer chain from the chromophore. The synthesis and electropolymerisation of two tetrakis(2-pyrrol-1-ylalkoxy)phthalocyanines are reported, and the electrical and optical properties of this new class of polymeric material are briefly discussed.

## Experimental

### Chemicals and equipment

All chemicals were used in the highest commercially available grade if not otherwise mentioned. For analysis of the prepared compounds the following equipment was used: FT-IR by Perkin-Elmer SP 1000, UV/Vis by Perkin Elmer Lambda 2 or 9, <sup>1</sup>H-NMR by Bruker DPX-200, MS by Finnigan MAT 8222. The electropolymerisations were carried out by use of a Jaissle T-NC connected to a Bank VSG 83 voltage scan generator and a Keithley DMM 2000 for computerised data acquisition. ITO (indium tin oxide) with an average thickness of 20 nm and a surface resistance of 200  $\Omega$  per square of Flachglas AG, Germany was used and cut into  $1 \times 1 \text{ cm}^2$  working electrodes. An Ag (purity 99.99%) wire served as a quasi-reference electrode and a  $1 \times 1 \text{ cm}^2$  Pt (purity 99.99%) foil as counter electrode. For vapour deposition of gold electrodes on top of the polymer films a high vacuum system of CJT (Germany) was used. Measurements of the conductivity were carried out with a Keithley 610 C electrometer connected to a Bank VSG 83 voltage scan generator. The light source for the photoconductivity measurements was a 1000 W xenon arc lamp (LOT Oriol) with glass and water filters to absorb UV and IR radiation.

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Average film thickness and average film roughness were determined by a Sloan Dektak III surface profiler and confirmed by a NTMDT SMENA atomic force microscope in the resonant mode using standard silicon tips.

**2-Pyrrol-1-ylethan-1-ol (1a).** 100 g (1.635 mol) 2-hydroxyethylamine was added under stirring to 180 ml glacial acetic acid and cooled by an ice water–sodium chloride mixture in such a way that the temperature of the solution was kept below 20 °C. Then 50 g (0.38 mol) 2,5-dimethoxytetrahydrofuran was added in one portion. Afterwards the acetic acid was distilled off. The residue was treated with 300 ml water and five times extracted with dichloromethane. The organic solution was treated three times with a saturated aqueous solution of sodium sulfate solution, and the dichloromethane was distilled off. Then the residue was stirred over night with a mixture of 60 ml methanol and 60 ml 20% aqueous sodium hydroxide. After treating with a saturated aqueous solution of sodium chloride and extraction with dichloromethane, the organic phase was separated, dried with calcium chloride and the solvent was distilled off. The resulting product was distilled at 42 °C under a vacuum of  $10^{-3}$  mbar. Yield 12.2 g (27%). IR (KBr)  $\nu/\text{cm}^{-1}$  3099, 2941, 1656, 1500, 1430, 1284, 1091, 1071, 983, 865, 730.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  6.75 (t, 2H), 6.21 (t, 2H), 4.02 (t, 2H), 3.83 (t, 2H). MS (EI)  $m/z$  111, 80, 18.

**3-Pyrrole-1-ylpropan-1-ol (1b).** This compound was prepared in analogy to **1b** employing 36 ml glacial acetic acid, 11 g (0.15 mol) 3-hydroxypropylamine (dissolved in 30 ml propanol), and 10 g (0.075 mol) 2,5-dimethoxytetrahydrofuran. The compound **1b** was purified by distillation at 49 °C under a vacuum of  $10^{-3}$  mbar. Yield 9.5 g (59%). IR (KBr)  $\nu/\text{cm}^{-1}$  3368, 3099, 2940, 2881, 1665, 1500, 1448, 1281, 1089, 1053, 966, 822, 724.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  6.71 (t, 2H), 6.19 (t, 2H), 4.06 (t, 2H), 3.63 (t, 2H), 2.01 (m, 2H). MS (EI)  $m/z$  125, 81, 53, 18.

**4-(2-Pyrrol-1-yethoxy)phthalonitrile (2a).** 4 g (0.03 mol) dried potassium carbonate, 2.7 g (0.025 mol) **1a** and 3.5 g (0.02 mol) 4-nitrophthalonitrile were added to 30 ml dry dimethyl sulfoxide under dry inert gas. The mixture was stirred for 10 days at RT, and again 4 g potassium carbonate was added after 3 days. Then 300 ml cold water was added and the pH adjusted by aqueous HCl to pH 7. The precipitated product was dissolved in acetone. The solution was stirred with 4 g of activated carbon for 4 h and then filtered. This charcoal treatment was repeated two times. Then a part of the acetone was distilled off and the crystals formed were isolated. Yield 2.6 g (44%). IR (KBr)  $\nu/\text{cm}^{-1}$  3430, 3101, 3078, 3039, 2973, 2939, 2888, 2229, 1601, 1487, 1253, 1091, 1033, 994, 734.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.71 (d, 1H), 7.43 (d, 1H), 7.21 (dd, 1H), 6.55 (t, 2H), 6.18 (t, 2H), 4.15 (t, 2H), 3.95 (t, 2H). MS (EI)  $m/z$  237, 81, 53.

**4-(3-Pyrrol-1-ylpropoxy)phthalonitrile (2b).** This compound was prepared in a similar synthesis to that described for **2a**. A mixture of 1.9 g (0.015 mol) **1b**, 1.7 g 4-nitrophthalonitrile and 2 g (0.015 mol) potassium carbonate were stirred in 30 ml DMSO for 2 weeks (an additional 2 g  $\text{K}_2\text{CO}_3$  was added after 3 days). Yield 0.8 g (32%). IR (KBr)  $\nu/\text{cm}^{-1}$  3435, 3095, 3070, 3046, 2979, 2932, 2898, 2231, 1598, 1492, 1256, 1090, 903, 849, 733.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.73 (d, 1H), 7.47 (d, 1H), 7.2 (dd, 1H), 6.63 (t, 2H), 6.17 (t, 2H), 4.14 (t, 2H), 3.95 (t, 2H), 2.28 (m, 2H). MS (EI)  $m/z$  251, 81, 53.

**Synthesis of metal-free or metal-containing 2,9,16,23-tetrakis(2-pyrrol-1-ylethoxy)phthalocyanines 3a and 2,9,16,23-tetrakis(2-pyrrol-1-ylpropoxy)phthalocyanines 3b.** A solution of 0.002 mol **2a** or **2b** in 20 ml dry (!) pentanol was heated under dry inert gas and refluxed. 10 mg lithium was added and the mixture was heated under reflux for 1 h. For the

preparation of metal-containing phthalocyanines, 0.0015 mol of a metal salt (zinc acetate dihydrate, cobalt acetate tetrahydrate or nickel sulfate of analytical grade) was added, and the mixture was heated for another hour. The pentanol was removed under vacuum, and the oily residue was treated for 1 h with a 1 : 1 mixture of water–methanol to remove unreacted metal acetates. In the case of the metal-free phthalocyanines, the products were treated for 10 min with an aqueous buffer solution of pH 5. The solid products were isolated, washed with water and treated in a Soxhlet apparatus with methanol to extract unreacted nitriles. Purity of the phthalocyanines are confirmed by thin layer chromatography.

**3a (M = 2H),** Yield 90%. IR (KBr)  $\nu/\text{cm}^{-1}$  3284, 3099, 2925, 2856, 1611, 1485, 1235, 1089, 938, 823, 725. MS (DCI,  $\text{NH}_3$ , negative)  $m/z$  950. UV/Vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda/\text{nm}$  701, 666, 640, 338, 287, 230.

**3a (M = Zn),** Yield 95%. IR (KBr)  $\nu/\text{cm}^{-1}$  3287, 3099, 2928, 2863, 1608, 1489, 1230, 1089, 945, 827, 728. MS (DCI,  $\text{NH}_3$ , negative)  $m/z$  1012. UV/Vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda/\text{nm}$  682, 615, 348, 264, 232.

**3a (M = Co),** Yield 97%. IR (KBr)  $\nu/\text{cm}^{-1}$  3322, 3078, 2928, 2878, 1601, 1487, 1188, 1089, 956, 864, 728. MS (DCI,  $\text{NH}_3$ , negative)  $m/z$  1007. UV/Vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda/\text{nm}$  671, 617, 326, 288, 226.

**3a (M = Ni),** Yield 85%. IR (KBr)  $\nu/\text{cm}^{-1}$  3324, 3081, 2937, 2878, 1610, 1418, 1239, 1093, 727, 667. MS (DCI,  $\text{NH}_3$ , negative)  $m/z$  1006. UV/Vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda/\text{nm}$  671, 619, 329, 279, 227.

**3b (M = 2H),** Yield 90%. IR (KBr)  $\nu/\text{cm}^{-1}$  3292, 3092, 2927, 2870, 1611, 1499, 1238, 1089, 969, 821, 723. MS (DCI,  $\text{NH}_3$ , negativ)  $m/z$  1007. UV/Vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda/\text{nm}$  703, 665, 641, 608, 341, 288.

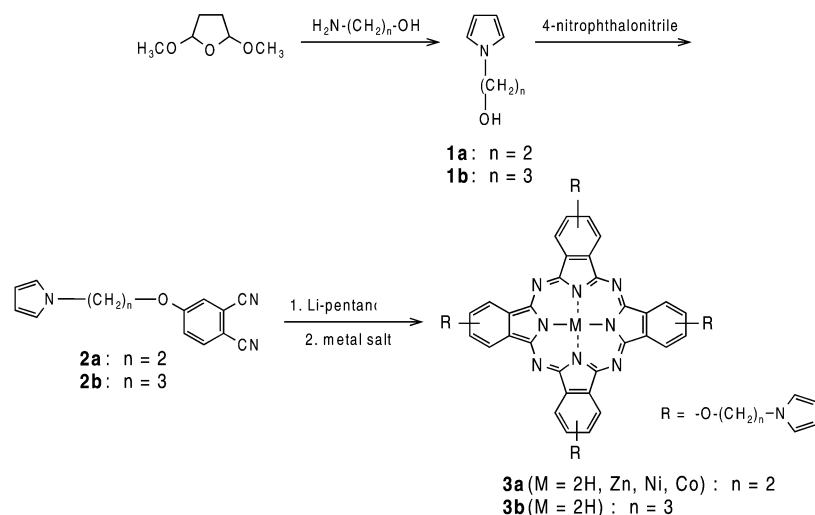
## Electropolymerisation

The electrochemical experiments were performed in a one-compartment glass cell (volume 3 ml) containing the ITO working electrode, a Ag wire as quasi-reference electrode and a Pt foil as counter electrode in a three-electrode arrangement. The potential of the Ag wire was calibrated by measurement of the ferrocene/ferrocenium reversible redox potential ( $E = 0.4$  V vs. SCE). This calibrated Ag wire was used as a quasi-reference instead of a regular reference electrode in order to avoid uncontrolled traces of water in the electrolyte. Before the measurement, the ITO electrode was cleaned by rinsing with water, distilled water and ethanol followed by drying under inert gas. The Pt electrode was cleaned in  $\text{H}_2\text{SO}_4\text{--H}_2\text{O}_2$  and the Ag wire by polishing and ultrasonic treatment in ethanol. All experiments were performed at room temperature under argon unless otherwise noted; potential values are reported relative to the SCE. The following standard conditions were used:  $5 \times 10^{-5}$  mol monomer in 5 ml 0.1 mol  $\text{l}^{-1}$  tetrabutylammonium hexafluorophosphate in dichloromethane. The electropolymerisations were carried out either under potentiodynamic conditions by scanning between 0.1 and 1.4 V vs. SCE at a scan rate of 10  $\text{mV s}^{-1}$  or at a fixed potential of 1.4 V vs. SCE.

## Results and discussion

### Synthesis of pyrrole substituted phthalocyanines

2,9,16,23-Tetrakis(pyrrol-1-ylethoxy)phthalocyanines **3a** with different central groups (M = 2H, Co, Ni or Zn) and 2,9,16,23-tetrakis(pyrrol-1-ylpropoxy)phthalocyanine **3b** (M = 2H) were synthesized by cyclotetramerisation of 4-(pyrrol-1-ylalkoxy)phthalonitriles **2a,b** in pentanol in the presence of Li pentanolate in almost quantitative yields (Scheme 1). Prior to this, the pyrrol-1-ylalkanols **1a,b** had to be prepared. The reaction of potassium pyrrolide with bromoalkanes<sup>23,24</sup> was not practical due to side reactions and a difficult work-up procedure. A



Scheme 1

method described by Caprio *et al.*<sup>25</sup> was used, and modified procedures for the synthesis of **1a,b** are described in the Experimental section. 2,5-Dimethoxyfuran was reacted with hydroxyalkylamines. In the reaction the amino group substitutes the oxygen in the furan ring, aromatization occurs and the methoxy groups are eliminated by heating. In the second step the nitro group in 4-nitrophthalonitrile is substituted by the nucleophilic HO-group of **1a,b** to obtain **2a,b** which are then converted to **3a,b** by the Li pentanolate method.

### Electropolymerisations

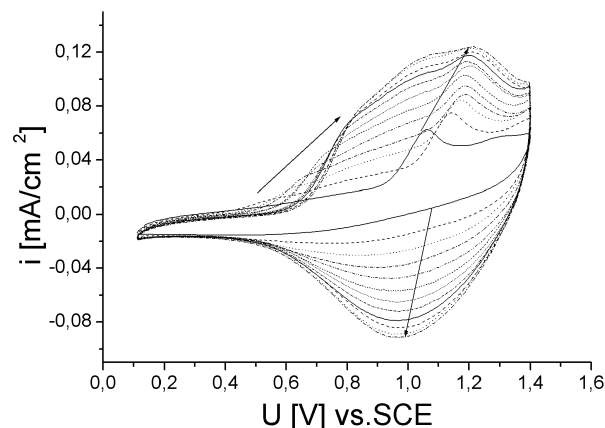
Upon reductive scanning, the pyrrole-substituted phthalocyanines display one reversible peak between  $-0.52$  and  $-1.1$  V vs. SCE (Table 1). These reductions can be attributed to a one-electron reduction of the phthalocyanine either at the ligand or, in the case of **3a** ( $M = Co$ ), at the cobalt(II) center.<sup>11</sup> Upon oxidative scanning below  $1.1$  V vs. SCE, the voltammograms of the monomers exhibit a first reversible one-electron peak ( $0 \times 1$ ) corresponding either to the ligand oxidation in the case of **3a,b** ( $M = 2H, Zn, Ni$ ) or the metal oxidation in the case of **3a** ( $M = Co$ ).<sup>11,19,20</sup> This first oxidation is followed by a second irreversible peak ( $0 \times 2$ ) at potentials more positive than  $1.2$  V vs. SCE (Table 1). For metal-free pyrrole-substituted porphyrins, it was shown earlier that irreversible oxidation peaks around  $1.0$  V vs. SCE corresponded to the irreversible oxidation of pyrrole with subsequent polymerisation whereas a reversible peak of  $\sim 0.4$  V vs. SCE was responsible for the porphyrin ligand oxidation.<sup>10,21,26</sup> In the case of 5,10,15,20-tetraaminophthalocyanines irreversible oxidation with subsequent polymerisation occurs at lower potentials of  $\sim 0.6$ – $0.9$  V vs. SCE. Since all the waves at lower potentials are assigned, it is consistent that the oxidative electropolymerisation of the

pyrrole-substituted phthalocyanines takes place at oxidation potentials of  $> 1.2$  V vs. SCE.

The film growth was studied at a scan rate of  $10$  mV s<sup>-1</sup> up to an overall cycling time of 2 h. Repeatedly scanning the potential between  $0.1$  and  $1.4$  V vs. SCE at first leads to an expected increase in the current due to a superposition of the redox activity of the deposited films and additional polymerisation. This increase of current is accompanied by a positive shift of the oxidation peak potentials as exemplarily shown for **3a** ( $M = Co$ ) in Fig. 1 for every 5<sup>th</sup> cycle. Table 1 contains the potentials for the oxidation of all investigated polymers formed on the electrodes after five cycles. It is seen that the oxidation of the polymers generally shifts to more positive potentials relative to the respective monomers which could either mean that the polymers are more difficult to oxidize when compared to their monomers or that the resistance of the film increases considerably and hence the oxidation potential at the film surface is reached at more positive potentials only. By a simultaneous, but smaller negative shift of the reduction peaks it is indicated that both the resistive loss within the films and a shift of the oxidation potential have to be considered. With a further increase of the number of potential scans the charge density within the cyclic voltammograms decreases slightly. It is thereby shown that the resistive loss within the films and the more difficult oxidation at the films lead to an incomplete reaction for thicker films. It can be concluded that the layer thickness obtained after 2 h of scanning under these standard conditions (Table 2) depends on the availability of the

**Table 1** Oxidation and reduction peaks in V vs. SCE of the phthalocyanines **3a,b** and their oligomers measured under potentiodynamic conditions

Phthalocyanine	$0 \times 1$	$0 \times 2$	Red1	Red2
Monomer <b>3a</b> ( $M = 2H$ )	0.73	1.20		-1.03
Oligomer of <b>3a</b> ( $M = 2H$ )	1.20	1.40		-1.05
Monomer <b>3a</b> ( $M = Zn$ )	0.67	$> 1.40$		-0.52
Oligomer of <b>3a</b> ( $M = Zn$ )	0.82	$> 1.40$		-0.56
Monomer <b>3a</b> ( $M = Ni$ )	1.05	1.30		-1.00
Oligomer of <b>3a</b> ( $M = Ni$ )	1.10	1.40		-1.00
Monomer <b>3a</b> ( $M = Co$ )	0.72	1.30		-0.69
Oligomer of <b>3a</b> ( $M = Co$ )	0.80	1.39		-0.75
Monomer <b>3b</b> ( $M = 2H$ )	0.91	1.34		-1.09
Oligomer of <b>3b</b> ( $M = 2H$ )	1.10	1.38		-1.10



**Fig. 1** Oxidative electropolymerisation of **3a** ( $M = Co$ ) under standard conditions by repeated potential scans (every 5<sup>th</sup> cycle up to 25 cycles shown).

**Table 2** Thickness, roughness, accommodated charge, yield of film formation and maxima in the optical absorption spectra of the polymer films of **3a,b**

Polymer from monomer	Method of electropolymerisation <sup>a</sup>	Thickness/nm	Roughness/nm	Accommodated charge/C	Yield of film formation/ $\mu\text{m}^{-1}\text{C}^{-1\text{b}}$	Electrons per monomer <sup>c</sup>	Vis maxima/nm <sup>d</sup>
<b>3a</b> (M = 2H)	A	3000	1200	0.18	16.7	3.7	624
	B	1900	400	0.30	6.3	9.9	663, 693, << 621
<b>3a</b> (M = Zn)	A	120	30	0.024	5.0	12.5	634 < 685
	B	120	10	0.020	6.0	10.4	634 < 685
<b>3a</b> (M = Ni)	A	80	60	0.049	1.6	39.1	680 < 630
	B	100	20	0.097	1.0	62.5	630
<b>3a</b> (M = Co)	A	810	60	0.021	38.6	1.6	674 < 612
	B	740	200	0.020	37.0	1.7	674 < 625
<b>3b</b> (M = 2H)	A	5050	1270	0.23	22.0	2.8	622
	B	2850	600	0.34	8.4	7.4	666 < 613

<sup>a</sup>A, at +1.4 V vs. SCE, B, during cyclic scanning between 0.1 V and 1.4 V vs. SCE at 10 mV s<sup>-1</sup>. <sup>b</sup>Ratio of the average film thickness and the accommodated charge. <sup>c</sup>Based on an assumed film density of 1.5 g mol<sup>-1</sup>. <sup>d</sup>The sign < represents increase of intensity of absorption maxima.

monomers (solubility and formation of insoluble intermediates), the reactivity of the monomers, the polymerisation yield of initially formed radical cations as opposed to side reactions in the electrolyte and also on the shift of the oxidation potential and the resistivity of the produced polymer films. Under the present experimental conditions the influence of these different parameters is difficult to distinguish but we can summarize an increasing overall reaction rate in the order **3a** (M = Ni), **3a** (M = Zn) < **3a** (M = Co) < **3a** (M = 2H) < **3b** (M = 2H). Table 2 compares the average film thickness and roughness obtained after 2 h of polymerisation. A constant potential of 1.4 V vs. SCE resulted in thicker films when compared with films prepared under cyclic scanning. This difference will mainly be caused by the additional need of ionic transport in the films during cyclic scanning, which is hindered in the films.

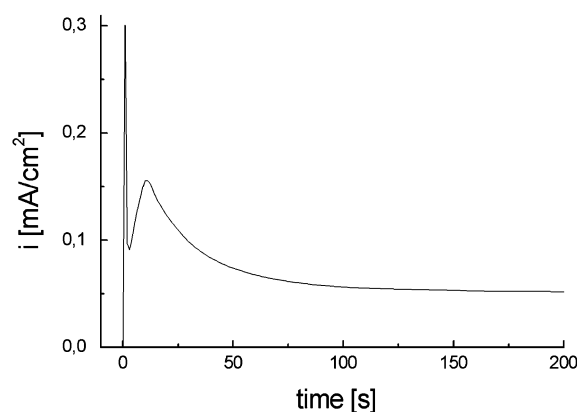
An interesting parameter of electrochemical reactivity is the current yield of film formation relative to oxidation reactions that do not lead to film formation, e.g., side reactions of the initially formed radical cations or oxidation of the electrolyte. As a measure of this parameter the ratio of average film thickness and consumed anodic charge is included in Table 2. It is clear that this parameter leads to a different ranking of the monomers when compared with the overall reaction rate as listed above since it is almost independent of monomer solubility and shifts in potential. When formation yields are compared according to the method of electropolymerisation it is seen that the largest differences are observed for the metal-free monomers. This coincides with their high overall reaction rate and hence the largest observed film thickness. Less positive potentials as widely present during cyclic scanning obviously either lead to an increased probability of side reactions or to less dense films. Both would be explained by a smaller probability of radical-radical annihilation and an increased probability for diffusion away from the electrode at less positive potentials. For the other materials growing at a significantly smaller current this difference seems to be less important.

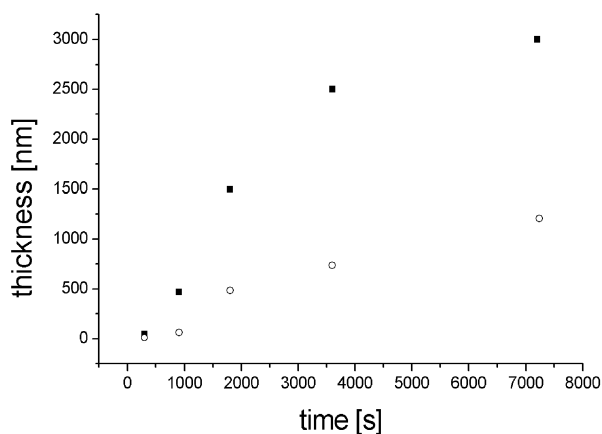
In spite of a considerably smaller current (leading to an overall smaller local concentration of radical cations), the polymerisation of **3a** (M = Co) shows clearly the highest yields of formation. Side reactions obviously play a minor role for this monomer. At a similar current **3a** (M = Zn) shows a significantly smaller formation yield whereas **3a** (M = Ni) shows a much smaller yield even at higher current. The formation yield (although determined at different overall reaction rate) increases in the order **3a** (M = Ni), **3a** (M = Zn) < **3a** (M = 2H) < **3b** (M = 2H) < < **3a** (M = Co). The comparison with the overall reaction rate shows that the latter is widely dominated by the reactivity of the monomers but that the reactivity of the Co complex of **3a** is widely underestimated judging from the overall reaction rate, probably caused by a

low solubility since its redox potential does not differ significantly from that of the other monomers. Since both metal-free complexes were completely soluble under the chosen polymerisation conditions, the increased yield of formation as well as the overall reaction rate indicate an increased reactivity of the radical cations if a longer spacer in **3b** in comparison to **3a** is used between the polymerisable group and the phthalocyanine chromophore which would increase spatial flexibility, which is beneficial for film formation.

In an approach similar to that used for the calculation of the yield of film formation, the number of electrons transferred at the electrode for each monomer unit can also be calculated if a density of approximately 1.5 g mol<sup>-1</sup> is assumed for the films. These values are also included in Table 2. In the limit of subsequent complete oxidation of all four pyrrole groups and the absence of any chain reactions, a value of four would be expected. If only one pyrrole group is oxidised in each monomer, and without consideration of chain reactions, the value would be one. This latter condition is roughly reached for the Co complex of **3a**. The metal-free **3a** and **3b** show values around four indicating complete oxidation. The Zn- and Ni-complexes of **3a** exhibit considerably higher values indicating significantly lower reactivity of the cation radicals produced for film formation, since oxidation by more than four electrons does not appear reasonable. None of the monomers shows values below one which would indicate true polymerisation chain reactions. This was expected, however, since electrochemical polymerisations, although following a radical mechanism, generally do not occur in chain reactions.

The film growth at a constant potential of 1.4 V vs. SCE was investigated in more detail. A characteristic change in the current with time was found which is exemplarily shown in Fig. 2 for the monomer **3a** (M = 2H). Following a first quick

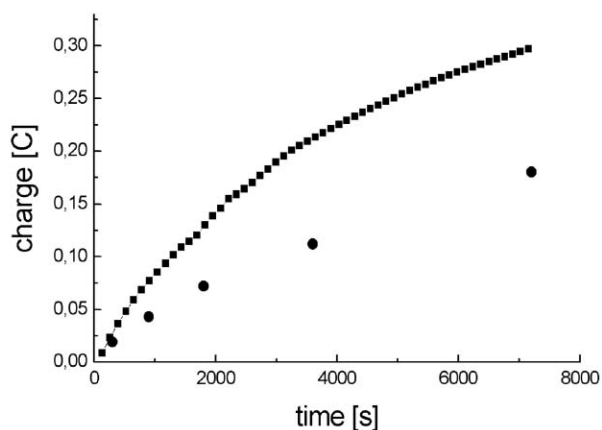
**Fig. 2** Time dependence of the current for the electropolymerisation of **3a** (M = 2H) under standard conditions at 1.4 V vs. SCE.



**Fig. 3** Time dependence of the polymer film thickness (■) and roughness (○) for the electropolymerisation of **3a** ( $M = 2H$ ) under standard conditions at 1.4 V vs. SCE.

maximum caused by capacitive charging of the electrode (capacity of the electrode 93  $\mu\text{F}$ ) faradaic currents caused by the oxidation of monomers, oligomers and subsequent polymerisation were observed. In an induction period the current increases which can be explained by seed formation of the polymers and a relative ease of growth of further polymer material on preformed polymer sites. Then the currents decrease continuously due to the increasing resistivity of the polymer film as also observed during cyclic scanning (see above). The polymerisation was stopped after different polymerisation times, and the film thickness and roughness were determined (Fig. 3). As expected from the change in the current, the film thickness also shows a saturation behavior with time. Fig. 4 contains the corresponding increase of the consumed charge with time. The higher charge (determined by integration of the currents over time) generally found for reactions at constant potential (see above) when compared with polymerisations under cyclic scanning is confirmed for short as well as longer reaction times. An almost constant linear correlation, however, is observed between the film thickness and the charge consumed during film growth which proves a generally constant yield of film formation during the time of reaction.

Aside from the parameters considered above, film growth by electrochemical polymerisation is also influenced by the kind of electrolyte as studied for the electropolymerisation of a number of monomers, including tetraaminophthalocyanine.<sup>11</sup> The monomer **3a** ( $M = 2H$ ) was therefore polymerised at 1.4 V vs. SCE under standard conditions using different supporting electrolytes in the solvent dichloromethane. With increasing

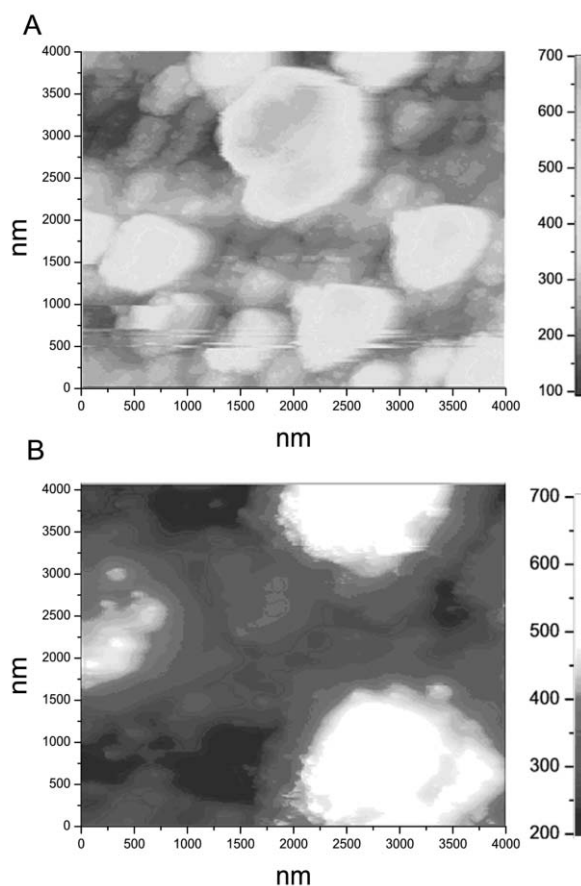


**Fig. 4** Time dependence of taken up charge for the electropolymerisation of **3a** ( $M = 2H$ ) potentiodynamically (■) and (●) under standard conditions.

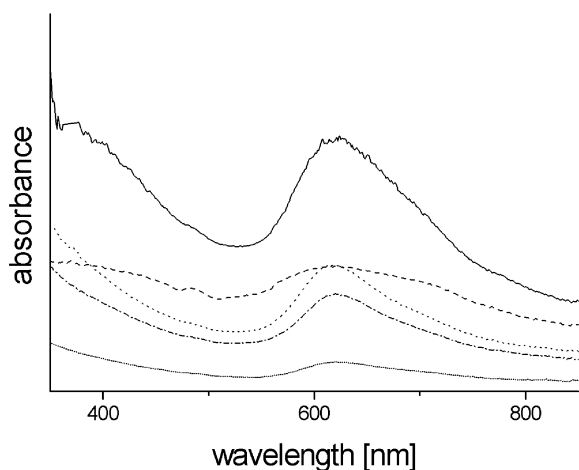
ionic radius of the anion, an increasing film thickness was obtained after 2 h, tetrabutylammonium tetrafluoroborate ( $1.46 \mu\text{m}$ ) < tetrabutylammonium perchlorate ( $2.7 \mu\text{m}$ ) < tetrabutylammonium hexafluorophosphate ( $3.0 \mu\text{m}$ ). The current was comparable in these experiments, and either an increased yield of film formation or a decreased density would be caused by the larger counter ions.

The film morphology was studied by AFM. As is typical for films prepared by electrochemical polymerisation, and also observed in the case of tetraaminophthalocyanine,<sup>11</sup> rough films were obtained (Table 2). The roughness reaches to around one third of the average film thickness. Fig. 5 exemplarily shows AFM images of films from **3a** ( $M = 2H$ ) obtained at a constant potential of 1.4 V vs. SCE after 5 min and also following 2 h of polymerisation. After 5 min polymer structures with a diameter of  $\sim 1 \mu\text{m}$  (average thickness  $\sim 0.2 \mu\text{m}$ ) are formed which increase to  $\sim 4 \mu\text{m}$  (average thickness  $3 \mu\text{m}$ ) after 2 h.

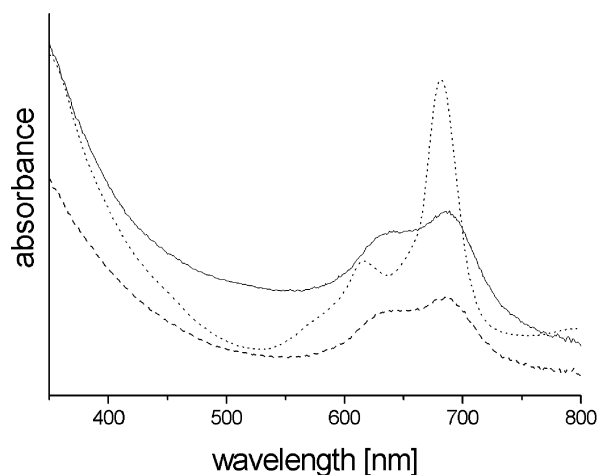
UV/Vis spectra are very useful to monitor the presence of phthalocyanine and polypyrrole subunits and interactions between them. The Q-band absorption occurs in all polymers between 690 and 610 nm (Table 2). An absorption decreasing almost linearly in intensity from 300 to 800 nm is characteristic for the brown-black-colored polypyrrole. The continuous increase in the absorptions of the phthalocyanine and polypyrrole is seen in Fig. 6. In Figs. 7 and 8 exemplarily the UV/Vis spectra of the polymers from **3a** ( $M = \text{Zn}, \text{Co}$ ) after 2 h under cyclic scanning or at constant potential are compared with spectra of the monomers in solution. In the case of **3a** ( $M = \text{Zn}$ ) the polymer spectra resemble mainly the spectrum of the monomer in solution which means that the phthalocyanine molecules are mainly distributed monomolecularly in the polypyrrole chains. On the other hand, the shift of the absorption



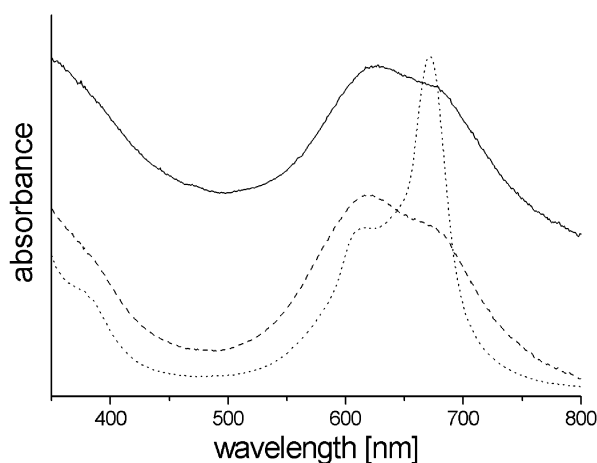
**Fig. 5** AFM images of films obtained by the electropolymerisation of **3a** ( $M = 2H$ ) under potentiostatic conditions. A, film after 5 min; B, film after 2 h.



**Fig. 6** UV/Vis transmission spectra of polymer films for the electropolymerisation of **3a** ( $M = 2H$ ) in dichloromethane containing tetrabutylammonium hexafluorophosphate under standard conditions at 1.4 V vs. SCE. Polymerisation time: — 5 min, - - - 15 min, ... 30 min, - · - · - 1 h, ——— 2 h.



**Fig. 7** UV/Vis transmission spectra of **3a** ( $M = Zn$ ) in dichloromethane and their polymers obtained after 2 h under standard conditions. ... in dichloromethane, — potentiodynamic polymerisation, - - - potentiostatic polymerisation, - · - · - potentiostatic polymerisation.



**Fig. 8** UV/Vis transmission spectra of **3a** ( $M = Co$ ) in dichloromethane and their polymers obtained after 2 h under standard conditions. ... in dichloromethane, — potentiodynamic polymerisation, - - - potentiostatic polymerisation, - · - · - potentiostatic polymerisation.

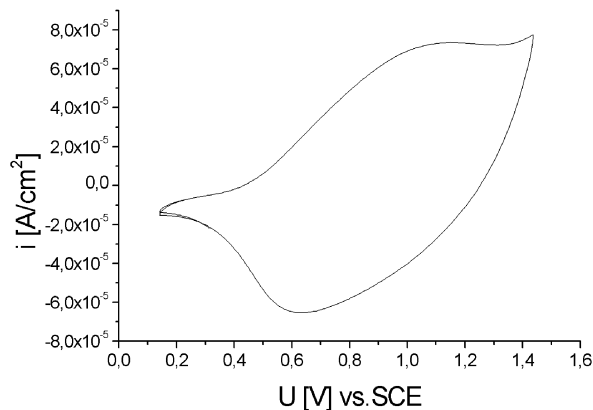
maximum in the polymers for **3a** ( $M = Co$ ) to 625 nm is characteristic of a phthalocyanine–phthalocyanine interaction with direct metal–metal contact in a sandwich orientation.<sup>1</sup> In most polymers absorptions at  $\sim 680$  and  $\sim 620$  nm show the presence of both monomolecular distributed and interacting phthalocyanines (Table 2). A different absorption behaviour was observed for polymers obtained by electropolymerisation of 2,9,16,23-tetraaminophthalocyanine.<sup>27</sup> In this case a continuous increase in the absorption from  $\sim 600$  nm to  $> 800$  nm shows that the phthalocyanine is involved in the conjugated pathways of the aminobenzene chains.

Charge/discharge and electrochromic behaviour were investigated for polymer films in contact with an inert electrolyte in the same cell as used for the electropolymerisation. The potential was scanned between 0.1 and 1.4 V vs. SCE in dichloromethane containing  $0.1 \text{ mol L}^{-1}$  tetrabutylammonium hexafluorophosphate under inert gas. Fig. 9 shows exemplarily the reversible charge/discharge behaviour of the electrode with a polymer film from the monomer **3a** ( $M = Co$ ). A redox potential of 0.86 V vs. SCE and a charge uptake of  $3.6 \times 10^{16}$  electrons were determined. Again assuming a density of  $1.5 \text{ g mol}^{-1}$  this corresponds to the oxidation and re-reduction of every second monomer unit.

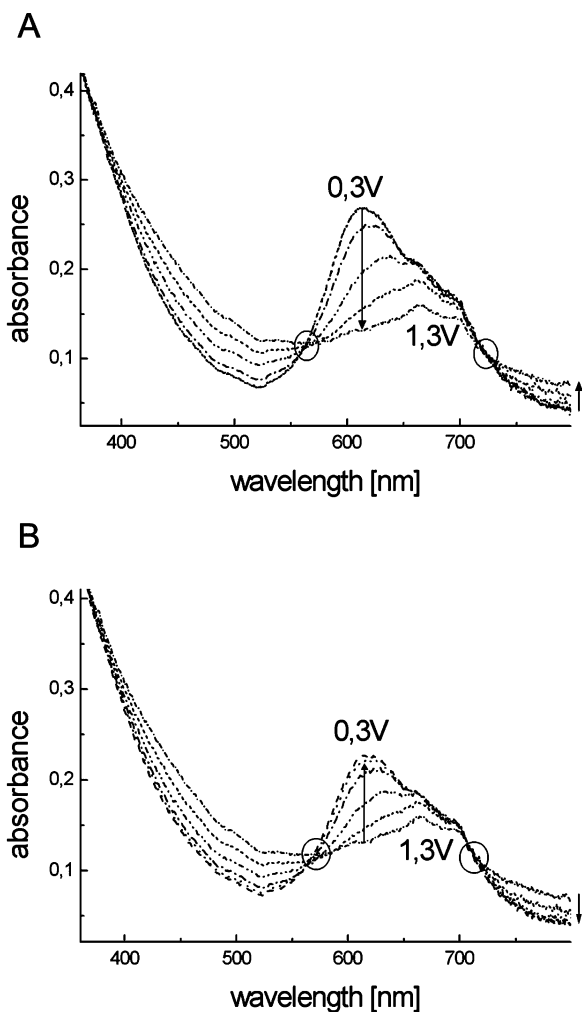
This oxidation and the re-reduction is clearly reflected in changes of the optical absorption spectra. One example for the electrochromic behaviour using the polymer film of **3a** ( $M = 2H$ ) is shown in Fig. 10. The oxidation at 1.3 V vs. SCE results in a decrease of the maximum at 620 nm and an increase of an absorption at 664 nm which is characteristic for the oxidation of the phthalocyanine (Fig. 10A).<sup>28</sup> A continuous increase of the absorption region  $> 750$  nm is typical for the oxidation of the pyrrole. Fig. 10B contains the absorption change by re-reduction, and two isosbestic points confirm the reversibility of the charge/discharge processes. Surprisingly, only one oxidation peak can be observed. A simultaneous reaction of the phthalocyanine and polypyrrole moieties occurring within the broad oxidation and re-reduction waves is thereby indicated. This reaction preferably occurs at the electrolyte/film interface, and the films are (not completely) oxidised and re-reduced as indicated by the optical spectra and the charge uptake.

### Conductivity

For the determination of the specific conductivities of the polymer films, the films obtained by electropolymerisation at 1.4 V vs. SCE were carefully washed with dichloromethane and dried. Four gold electrodes of 30 nm thickness (diameter 3 mm, distance 2 mm) were vapor deposited through a mask under a vacuum of  $10^{-5}$  mbar. Current–voltage plots between  $-1$  V and  $+1$  V were measured between two of the different gold



**Fig. 9** Cyclic voltammogram of a polymer film prepared from **3a** ( $M = Co$ ) under potentiodynamic conditions. Measurements in dichloromethane containing  $0.1 \text{ mol L}^{-1}$  tetrabutylammonium hexafluorophosphate. Scan rate  $10 \text{ mV s}^{-1}$ .



**Fig. 10** UV/Vis spectra of a polymer film prepared from **3a** ( $M = 2H$ ) under potentiodynamic conditions. Measurements in dichloromethane containing  $0.1 \text{ mol L}^{-1}$  tetrabutylammonium hexafluorophosphate at a potential as indicated in the graph.

electrodes under air. The conductivity through the film using the ITO substrate as the second electrode was also measured for some films but inhomogeneities in the films even leading to pinholes in the films often prevented us from obtaining reliable results. The conductivities were determined from the slopes of the  $V$ - $I$  plots as average values of different measurements and the specific conductivities were estimated based on the average film thickness and the geometric surface area. When compared with the films of the metal-containing monomers, the thicker films of the polymers prepared from **3a** and **3b** ( $M = 2H$ ) (Table 2) gave the most reliable values since they consisted of a widely closed morphology and had no short circuits. The following specific conductivities were determined, **3a** ( $M = 2H$ )  $\sigma = 1.9 \times 10^{-5}$ , **3b** ( $M = 2H$ ),  $\sigma = 1.2 \times 10^{-5} \text{ S cm}^{-1}$ . The conductivities are lower compared with polymers prepared by the electropolymerisation of 2,9,16,23-tetraaminophthalocyanines with  $\sigma \sim 3 \text{ S cm}^{-1}$ .<sup>27</sup> In that case the phthalocyanine, however, is part of the conjugated polymer system which obviously supports the conductivity in such composite polymers. Nevertheless a coupling of the electronic systems could also be shown in the present examples since the conductivities of both films increased by around one order of magnitude under illumination with white light of  $100 \text{ mW cm}^{-2}$  which demonstrates a photoconducting behaviour. More detailed

investigations on conductivities of the described polymers and related systems are on the way.

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