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Synthesis and electrochemical study of a tetra(ester thiophene)calix[4]arene: ionic recognition and electropolymerisation behaviour

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An electropolymerisable tetra ester calix[4]arene derivative **1** bearing four thiophene units appended at the lower rim has been synthesised. The oxidative behaviour and the ability of **1** to recognise alkaline and ammonium cations in acetonitrile solution was examined by cyclic voltammetry. The data are interpreted on the basis of the electroactivity of the four thiophene moieties as well as the electroactivity of the 2,6-disubstituted aryl ether moieties of **1**. Electrochemical homopolymerisation of **1** was achieved but produced electrochemically unstable films. Electrochemical copolymerisation of **1** with 3-methylthiophene (3-MeT) was investigated. The [3-MeT]/[**1**] ratio was observed to influence the electrochemical stability and recognition ability for sodium cations of the resulting films.

1. Introduction

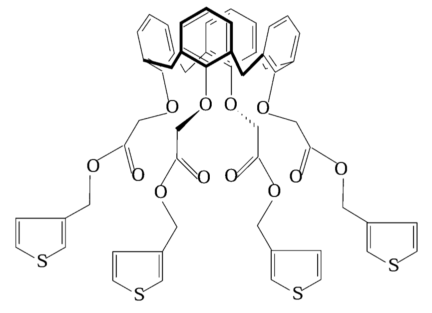
Calixarenes are recognised as the third class of macrocyclic host molecules after crown ethers and cyclodextrins.[1–3] These metacyclophanes, resulting from the condensation of phenols with formaldehyde, can be synthesised with a variety of ring sizes and offer scope for a broad range of derivatives functionalised at either the upper or the lower rims, leading to an almost unlimited array of calixarene-based molecular or ionic receptors.

Combination of such receptors with well-known electroactive moieties such as ferrocene, cobalticinium or quinones, for example, has already led to many examples of electroactive receptors. These have facilitated the electrochemical recognition of many different chemical species in solution.[4] The electrochemical detection of the recognition process can occur in these bifunctional receptors only if the electroactivity of the reporter redox-active group is influenced by intramolecular perturbations resulting from a host–guest complex formation.[5]

Immobilisation of bifunctional electroactive receptors at an electrode surface can lead to development of amperometric sensors if the electrochemical recognition ability existing in solution is conserved after immobilisation. Bifunctional redox-active receptors bearing electropolymerisable units, *e.g.* pyrrole or thiophene, lead to trifunctional molecules that can be electrodeposited onto the electrode surface (*e.g.*refs. 6 and 7) *via* electropolymerisation and the formation of conducting polymers.[8] Indeed, since conducting polymers are electroactive, they can replace the electroactive signalling unit of the bifunctional receptor. This allows the use of bifunctional molecules possessing a binding site in close proximity to an electropolymerisable unit.[9]

It has been recently shown that chemically synthesised polythiophenes functionalised with calix[4]arene-based ion receptors lead to a successful transduction of the calixarene guest recognition process, resulting from change(s) in the polymeric matrix electroactivity.[10] Following this result, several papers targeting the electrochemical polymerisation of calixarene-based electropolymerisable receptors have been reported.[11–14]

We are interested in the applications of calixarenes in sensors and analytical devices.[15] With the aim of preparing recognition films *via* electropolymerisation of suitably functionalised receptors, we have synthesised a new electropolymerisable calixarene-based receptor, **1**. The bulkiness of this compound has been minimised by the use of the electropolymerisable thiophene units as the signalling units rather than employing an additional signalling unit. The thiophenes can act as signal units either in solution or incorporated into polythiophene chains. We report here our investigations into the synthesis, electrochemical behaviour, recognition properties towards selected cations and electropolymerisation of this compound in non-aqueous solution.



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2. Experimental

2.1. Synthesis for compound 1

Compound **1** was synthesised as follows: 3-thienylmethyl-2-chloroacetate (0.017 mol) was reacted with dealkylated calix[4]arene (2.8 mmol) in the presence of NaI (0.018 mmol) and K_2CO_3 (0.017 mol) in dry acetone under N_2 and reflux. The reaction was monitored by thin-layer chromatography (hexane : ethyl acetate, 75 : 25). Heating was continued for 7 days. The mixture was then cooled to room temperature,

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filtered through Celite, washed with acetone and concentrated. The residue was redissolved in dichloromethane and the yellow solution washed with sodium thiosulfate solution (0.1 N, 2 × 50 cm^3) and then distilled water (2 × 50 cm^3) and back extracted with dichloromethane. This organic phase was then dried with magnesium sulfate and concentrated to give a yellow orange oil, which was pumped under high vacuum for 4 hours. The crude mixture was purified by column chromatography (flash silica, hexane : ethyl acetate, 8 : 2). The product **1** was isolated as a pale yellow semi-solid, 40% yield. Spectroscopic characteristics: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22 (m, ArH, thio H, 8H), 7.04 (m, ArH, thio H, 4H), 6.60 (m, ArH, calix H, 12H), 5.12 (s, OCH_2Ar, 8H), 4.79 (d, $ArCH_2Ar$, 4H, J = 13.7 Hz), 4.72 (s, OCH_2CO, 8H), 3.16 (d, $ArCH_2Ar$, 4H, J = 13.8 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 31.83 ($ArCH_2Ar$), 61.69 (CH_2CO), 71.60 (OCH_2Ar), 123.280, 124.89, 126.53, 128.09, 128.95, 134.93, 136.998 (ArC) 156.17 (ArC–O), 170.35 (C=O). IR (KBr, cm^{-1}): 1757 (C=O st.). MS (ES): *m*/*z* 1063 ($M^+ + Na^+$).

2.2. Electrochemical studies

Acetonitrile (hplc grade) was used for all electrochemical experiments. Potassium perchlorate, sodium perchlorate, ammonium perchlorate, lithium perchlorate and tetrabutyl ammonium perchlorate (TBAP) were of analytical grade, purchased from local suppliers and used as received. When necessary, increasing amounts of the perchlorate salt of the target cation were added to the electrolyte solutions (CH_3CN + TBAP (0.1 M)) of **1** by addition of small volumes of a stock solution with a micropipette.

Electrochemical studies were performed with an Oxford Electrodes portable potentiostat and triangular wave generator (Oxford, UK) coupled to an XY recorder (Recorderlab 60000, Surrey, UK) connected to a three electrode voltammetric minicell, 1 cm^3 volume, containing Pt pseudo-reference and counter electrodes sealed in the wall of the glass cell. The half-wave potential of ferrocene *versus* the Pt quasi-reference electrode was 0.175 V. All potentials are reported with respect to the ferrocene half-wave potential, unless stated otherwise. The working electrode was a 1.6 mm diameter Pt disc (BAS Technicol, Congleton, UK). This was polished with an aqueous alumina suspension and then cycled in 0.1 M H_2SO_4 until a stable voltammogram for oxide formation/reduction and hydrogen adsorption/desorption was obtained. The electrode was then rinsed in water, followed by acetonitrile and allowed to dry in air before use.

3. Results and discussion

3.1. Synthesis of 1

Compound **1**, tetraethyl ester thiophene *p*-*tert*-butyl calix[4]arene was synthesised by coupling of the 3-thiophene chloroacetate with the de-*tert*-butylated calix[4]arene in the presence of sodium iodide and potassium carbonate. The pure product **1** was obtained as an oily yellow semi-solid in 40% yield. The NMR and infrared spectra of this compound were consistent with the cone conformation of the calixarene moiety. It is thus optimally oriented for complexation of sodium cations. The attachment of the thiophene moieties, which makes this compound amenable to electropolymerisation, has therefore not distorted the molecular conformation.

3.2. Electrochemistry of 1

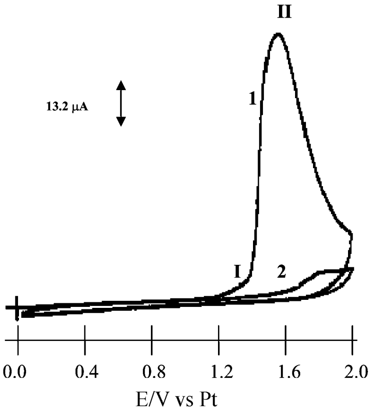
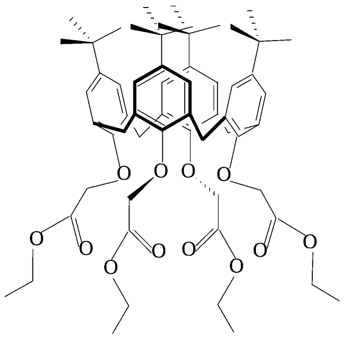


Fig. 1 Cyclic voltammogramm of **1** (1.05 × 10^{-2} M) in an electrolytic solution (0.1 M TBAP + CH_3CN) between 0 and 2.0 V. Scan rate: 200 mV s^{-1}.

The electrochemical behaviour of **1** was investigated by cyclic voltammetry (CV) in acetonitrile containing 0.1 M (TBAP). A typical CV (see Fig. 1) shows a shoulder (labelled I, $E_I \approx$ 1.35 V *vs.* Pt) followed by an irreversible and intense peak (labelled II, $E_{pII} \approx$ 1.60 V *vs.* Pt) in the potential region between 0 and 2.0 V. The oxidation of one or several of the 3-substituted thiophene units of **1** is likely to be involved in this electroactivity since the oxidation of 3-methylthiophene (3-MeT), also irreversible, was found to commence close to 1.30 V *vs.* Pt under similar experimental conditions. The simultaneous oxidation of the four thiophene units of **1** cannot be ruled out unless there are strong electronic repulsions between the four radical cations, as Beer *et al.* observed between three ferrocene units appended to the lower rim of a calix[5]arene derivative.[16] In any case, the electroactivity of the aryl ether moieties of **1** must also be considered. The aryl ether-based electroactivity of the tetraester *p*-*tert*-butyl calix[4]arene **2**, a structural precursor of **1**, has been observed recently.[17] Although the electroactivity of **2** was observed as a roughly step-shaped CV showing three consecutive irreversible oxidation waves between 0 and 2.0 V (see Fig. 1 in ref. 17), **1** shows a peak-shaped electroactivity (Fig. 1). Moreover, the value measured for the anodic current at E = 2.0 V in Fig. 1 is very close to the one expected in a blank solution and therefore much lower than the one measured during the CV of the aryl ether moieties[17] assuming that **1** and **2** have similar diffusion coefficients (see Fig. 1 in ref. 17). By comparison with the first oxidation process observed for **2**, the shoulder oxidation wave observed in Fig. 1 might indicate that one of the aryl ether moieties is oxidised first.



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Both the irreversibility of the oxidation peak II observed in Fig. 1 and the almost complete passivation of the platinum electrode surface, as revealed by the second anodic scan in Fig. 1, indicate that a chemical process has occurred involving the oxidation products of **1**. This led to the electrodeposition of an insulating and insoluble film on the working electrode surface. Consecutive potential cycling over the potential encompassing the three redox processes observed for **2** did not lead to any electrode passivation.[17] The chemical coupling of the thiophene radical cations of oxidised **1**, *via* either intra- or inter-molecular reactions with each other or with the *para* position of the unsubstituted, oxidised aryl ether units of other monomers, may lead to the formation of an insulating film. No new electroactivity due to a homopolymerisation process of **1** was observed in the experimental conditions used for Fig. 1, indicating that a conducting film of poly(**1**) is either not formed or is overoxidised within the potential range used for the experiments in Fig. 1. Nevertheless, the electrochemical activity of **1** was clearly demonstrated.

3.3. Electrochemical homopolymerisation of 1

The use of a lower positive potential limit than that employed in Fig. 1 for the CV of **1** leads to the production of a conducting polymeric film (Fig. 2). This also confirms the thiophene units of **1** are oxidised during the redox process labelled II illustrated in Fig. 1. Some of the main characteristics of the electrodeposition of a conducting polymer on an electrode surface, namely a nucleation loop and an increase of the monomer oxidation peak intensity during CV experiments, were not observed in repetitive CV studies of the homopolymerisation of **1** (Fig. 2). However, the appearance of a new, growing, reversible redox system at a potential less positive than that of monomer oxidation was indicative of the electrochemical deposition of a conducting film. A poly(**1**) film was thus believed to form, as shown by the growth of a new quasi-reversible wave (E_{pa} = 1.0–1.2 V, E_{pc} = 0.9 V *vs.* Pt). The intensity of this wave increased during several consecutive potentiodynamic cycles. This was in good agreement with the well known electrochemical deposition of conducting polymer films of increasing thickness such as polythiophene or poly(3-methylthiophene).[8,18–21] This new redox system was attributed to the oxidation/reduction (doping/dedoping) process of the new polymeric film. Even so, the shift in peak potential and the eventual decrease of the peak current observed for the new redox process on subsequent cycles, as well as the decrease of the oxidation current of the monomer, (Fig. 2), all indicated that the poly(**1**) film was unstable, unlike polythiophene or poly(3-methylthiophene) films. Of course the decrease in current and shift of peak potential might also be attributable to slow counter-anion movement in the growing polymeric film. The use of a high scan rate (1000 mV s^{-1}) was necessary for these experiments in order to obtain the film growth recorded in Fig. 2. This made possible an increased number of cycles for the growth, as well as increasing the current intensity of the new redox system, making the changes on consecutive cycles more visible. The features evident in Fig. 2 correspond to a polymeric film growth that is limited by the unstable electroactivity of the film.

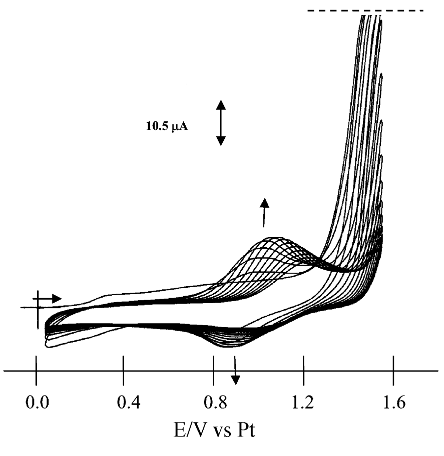

Fig. 2 Consecutive cyclic voltammogramms in an electrolytic solution (0.1 M TBAP + CH_3CN) of **1** (9.30 × 10^{-2} M) between 0 and 1.55 V. Scan rate: 1000 mV s^{-1}. The arrows indicate the direction of growth of the new wave.

This loss of electroactivity can be due either to a loss of planarity of the polymeric chains or to the presence of an increasing amount of disruption to the conjugation in poly(**1**) chains. Factors which can contribute to this behaviour are the inclusion of the bulky calix[4]arene unit and the coupling of the thiophene radical cations with the oxidised aryl ether moieties which are unsubstituted at the *para* position.

3.4. Solution-phase recognition of alkali metal and ammonium cations by 1

Previously, we have shown that the recognition of Li^+, Na^+, K^+ or NH_4^+ cations was possible using the electroactivity of the aryl ether moieties of **2**.[17] Since **1** and **2** bear similar binding sites, the cations listed above, which form 1 : 1 complexes with **2**, were therefore also expected to form complexes with **1**. This likely complex formation between **1** and the target cations was aimed at allowing the electrochemical recognition in solution of the four targeted cations. This recognition event could be based on either or both of the possible electrochemical processes attributed to the functional groups present in **1**: thiophene electro-oxidation or aryl ether electro-oxidation.

In order to assess these expectations, increasing amounts of the perchlorate salt of the targeted cations (Li^+, Na^+, K^+ or NH_4^+) were added to the electrolyte solution (CH_3CN + TBAP (0.1 M)) of **1** (*ca.* 10^{-2} M) in the electrochemical cell. After each new addition, CVs were recorded using a clean platinum electrode. As shown in Fig. 3(a) in the case of the sodium cation addition, the electrochemical behaviour of **1** was strongly modified by the increased concentration of the ions. In the first range of sodium cation additions, a progressive decrease of the current intensity for oxidation of **1** was observed. Further additions of the cation led to a split of the peak into two less intense oxidation peaks. During consecutive additions of lithium or potassium cations, qualitatively similar phenomenona were observed (Figs. 3(b) and 3(c) respectively). Addition of ammonium cations influenced the intensity but not the shape of the initial peak.

Several contributing factors may explain these observations: a change in the nature of the electrolyte, dilution of the receptor **1**, or complexation. Taking into account the small volume of the electrolyte solution in the electrochemical cell (1 cm^3), additions of the salts described above alter the concentration and identity of the background electrolyte solution. Control experiments with ferrocene in place of **1** indicated that any variation of the current values or peak shape for the oxidation of **1** observed during consecutive additions of perchlorate salts of the target cations was due either to a dilution affect or to complex formation.

In order to compare the current variations observed during the additions of any of the cations, the anodic peak current for the oxidation of **1** was measured and divided by the anodic peak current measured in the absence of cations, to produce a normalised anodic current independent of the initial monomer concentration. After a further calculation to correct for the dilution effect, a *corrected normalized current* I_{CN} was obtained and plotted *versus* the number of equivalents of the cations added (Fig. 4). From this figure, two kinds of behaviour are observed. When increasing amounts of Li^+ or Na^+ cations are added to the solution of **1**, the anodic current decreases for the initial equivalents of cations and then maintains a nearly constant value upon further additions. In the case of K^+ or NH_4^+ cations, the anodic current generally increases during the addition of the several equivalents. Note that it is at >1 added equivalents that the current becomes independent of numbers of equivalents added for both types of behaviour.

In a separate experiment, an excess of Na^+ cations (3.8 equivalents) was added to an electrolyte solution of **1**. An alteration of the voltammogramm identical to that observed in Fig. 3(a) for the same amount of cations was obtained. The

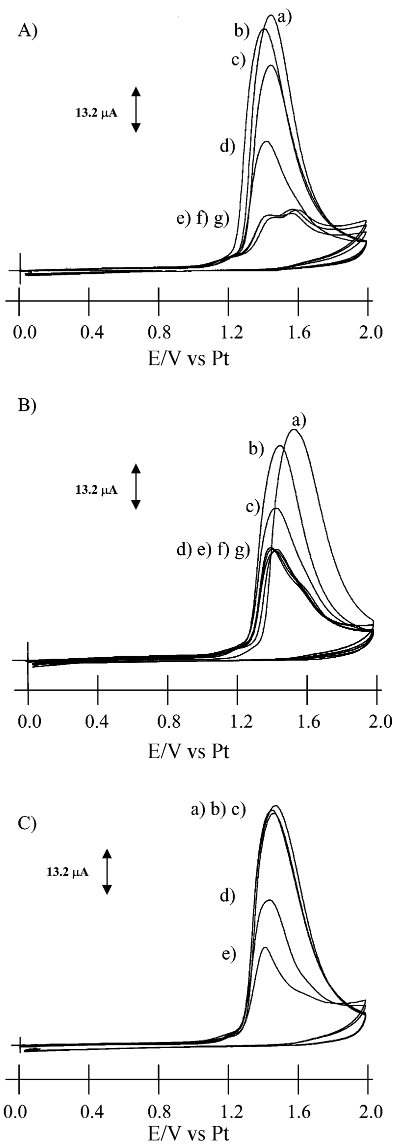

Fig. 3 A) Cyclic voltammogramms following additions of sodium cations to an electrolyte solution (0.1 M TBAP + CH_3CN) of **1** (1.18×10^{-2} M). Scan rate: 100 mV s^{-1}. Equivalents of Na^+: a) 0, b) 0.48, c) 0.96, d) 1.44, e) 3.37, f) 5.29, g) 7.22. B) Cyclic voltammogramms following additions of lithium cations in an electrolyte solution (0.1 M TBAP + CH_3CN) of **1** (1.05×10^{-2} M). Scan rate: 100 mV s^{-1}. Equivalents of [Li^+]: a) 0, b) 0.54, c) 1.09, d) 1.63, e) 3.81, f) 5.98, g) 8.16. C) Cyclic voltammogramms following additions of potassium cations in an electrolyte solution (0.1 M TBAP + CH_3CN) of **1** (9.57×10^{-3} M). Scan rate = 100 mV s^{-1}. Equivalents of [K^+]: a) 0, b) 0.50, c) 0.99, d) 1.49, e) 3.48.

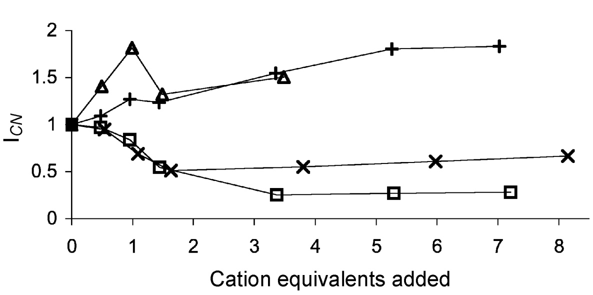

Fig. 4 Variation of the corrected normalised anodic peak current, I_{CN}, of **1** as a function of the amount of added cation: + = NH_4^+, △ = K^+, × = Li^+, □ = Na^+.

resulting CV was not altered by further additions of sodium perchlorate. Interestingly, a second, consecutive anodic scan at the same electrode (*i.e.* not cleaned in between) led to disappearance of the first anodic peak while the second was still observed although much less intense. Furthermore, it was observed that the shape of the initial CV observed for a solution containing **1** was not modified by the addition of seven equivalents of NH_4^+ but became similar to those observed in Fig. 3(a) following the addition of Na^+ cations (4.26 equivalents). This indicates that the presence of ammonium cations had no effect on the role of sodium cations in the perturbation of the electrochemical behaviour of **1**. It also shows that **1** retained the well-known Na^+-selectivity over NH_4^+ cations for tetra ester calix[4]arenes.

An electrochemical recognition phenomenon is usually observed in an electroactive receptor capable of coupling its complexation event to a redox reaction *via* one or more of five coupling pathways: through space electrostatic interaction, through bond electrostatic interaction, direct coordination of a guest by a redox-active component of the recognition site, conformational change on binding, or disruption of communication on binding (interference mechanism).[5] All the observations presented above can be explained from a coupling between the expected complex **1**Na^+ and the electroactive moieties of **1**. Investigations of the electrochemical recognition phenomenon of alkali cations by **2** have already shown that complex formation makes the electrochemical oxidation of aryl ether moieties of **2** more difficult.[17] This was explained from a likely electron withdrawing effect of the guest cation on the phenolic oxygen atoms known to be involved in ion binding. Such an electronic effect of the cation bound in **1** may explain the decrease of the initial peak observed in Fig. 3 and possibly the appearance of a new peak.

Nevertheless, a transfer of the perturbations due to the complexation phenomenon from the binding site to the thiophene units *via* through-space electrostatic interactions can also be considered. It obviously depends on the ionic diameter of the target cation compared with the length of the oxaalkyl chain separating the binding site from the electroactive thiophene unit. A binding of the targeted species may also have an influence on the flexing movement of the pendant ligating groups and/or a change in the tilt of the phenolic rings. Such influence would cause a perturbation of any interactions between the thiophene units. A similar interaction between three oxidisable ferrocene groups (which are bulkier than the thiophene moieties) appended to a calix[5]arene *via* short carboxyl groups has already been observed.[14] If this reasoning is accepted, the variation of the anodic current observed (Figs. 3 and 4) might be considered as a change of the number of simultaneously oxidisable thiophene moieties in **1** resulting from the binding of the target cation. Such a change would be a function of the size of the complexed cation. The binding of the smaller cations, Li^+ and Na^+, by **1** would result in a closer proximity of the thiophene groups making more unlikely and difficult the simultaneous oxidation of several of them. On the other hand, the binding of larger cations, K^+ and NH_4^+, could be responsible for a greater through-space separation of the thiophene units. This latter case would allow the simultaneous oxidation of more of the thiophene units in the complexes involving these cations than in the free ligand **1**. Note that the data in Fig. 4 are normalised with respect to the current of the uncomplexed **1**. The greater current ratios for K^+ and NH_4^+ indicate that more of the thiophenes are simultaneously oxidised in the presence of these ions than in the uncomplexed **1**.

Additionally, it must be considered that the oxidation of one or several thiophene units in the complexed form of **1** produces a polycationic complex. Indeed, the cationic guest may interact with the cationic oxidised thiophene units. These interactions, which vary with the size of the cation bound, might explain the appearance of a new oxidation peak at a higher potential, as shown in Fig. 3(a) for the complex of **1** with the Na^+ cations. This new process would be due to a more difficult oxidation of the thiophene groups that have not been oxidised during the first oxidation step. Such an observation for Li^+ ions supports this also; *i.e.* an additional shoulder is observed in Fig. 3(b) on addition of Li^+. Thus the smaller ions result in a closer proximity of the thiophene units, post-complexation, than do the larger cations, leading to the appearance of a new peak.

3.5. Electrochemical copolymerisation of 1 with 3-methylthiophene

Since the above results confirm the ability of **1** to recognise the target cations in solution, it was necessary to improve on the results obtained from the electrochemical homopolymerisation experiments. Obtaining a stable electropolymerised film of poly(**1**) is a key step in the fabrication of an ion detection device using poly(**1**) films as the sensing material.

Copolymerisation of **1** with 3-methylthiophene (3-MeT) has thus been studied as a means of preparing a stable film exhibiting calixarene-based ion-recognition capability. During these studies, it became clear that the [3-MeT]/[**1**] ratio controls the electro-copolymerisation process (Fig. 5). Firstly, it was observed that the presence of **1** in the copolymerisation solution makes the polymer growth systematically slower than that observed with the same concentration of 3-MeT in the absence of **1**. This indicates that **1** is involved in the polymer growth, probably *via* an inter-coupling between the 3-MeT radicals and the 3-substituted thiophene units of **1**. This provides evidence for a copolymer growth. Moreover, if the [3-MeT]/[**1**] ratio is very high (Fig. 5(C)), the copolymerisation process produces a very stable film growth similar to the one usually observed for poly(3-MeT) films. Unfortunately, the transfer of such films to an electrolyte solution containing either sodium perchlorate or tetrabutyl ammonium perchlorate as background salt does not reveal any perturbation of the film electroactivity by the cation. This might be due to an insufficient amount of **1** in the copolymer film.

In the opposite case of low [3-MeT]/[**1**] ratios (Fig. 5(A)), the film growth process was close to the highly limited growth observed during the electrochemical homopolymerisation of **1**. The transfer of the resulting films to a TBAP electrolyte solution showed a very quick degradation of the film electroactivity upon repetitive potential cycling encompassing the doping/dedoping redox process of the copolymer. Such degradation might be due to a loss of planarity of the copolymeric chains induced by the bulky **1** molecules, or due to slow counter-anion movement in the growing films. These same films were then transferred into a sodium perchlorate electrolyte solution. The first scan recorded after this transfer showed an anodic current that was clearly higher than the one measured on the last scan in TBAP. However, further ion-recognition studies with these copolymeric films are required.

4. Conclusion

The synthesis and electrochemical behaviour of a calixarene tetra-ester bearing four thiophene appendages has been undertaken. The ability of this tetra-ester thiophene calix[4]arene to be used in the electrochemical recognition of alkali metal and ammonium cations in acetonitrile solution was confirmed. The complexation/recognition phenomenon can be considered to be reliant on (i) the electrochemical behaviour of the aryl ether moieties of **1**, (ii) the electrochemical behaviour of the simultaneously oxidisable thiophene moieties in **1** and (iii) the polycationic nature of the oxidised complex. The electrochemical homopolymerisation of **1** was observed, with the typical evidence for conductive film growth being present, *i.e.* the appearance of a new redox process at a lower potential than that for monomer oxidation; however, the films so produced were electrochemically unstable. Electrochemical copolymerisation of **1** with 3-methylthiophene was also undertaken. The [3-Me-T]/[**1**] ratio controlled the stability of the resulting films as well as their electrochemical recognition properties towards the target cations. Unlike high ratios, low [3-Me T]/[**1**] ratios lead to unstable films that exhibited interesting electrochemically measurable interactions with sodium cations. The consideration of these observations will benefit the design of new electropolymerisable calixarene based receptors for the fabrication of calixarene-based amperometric sensors.

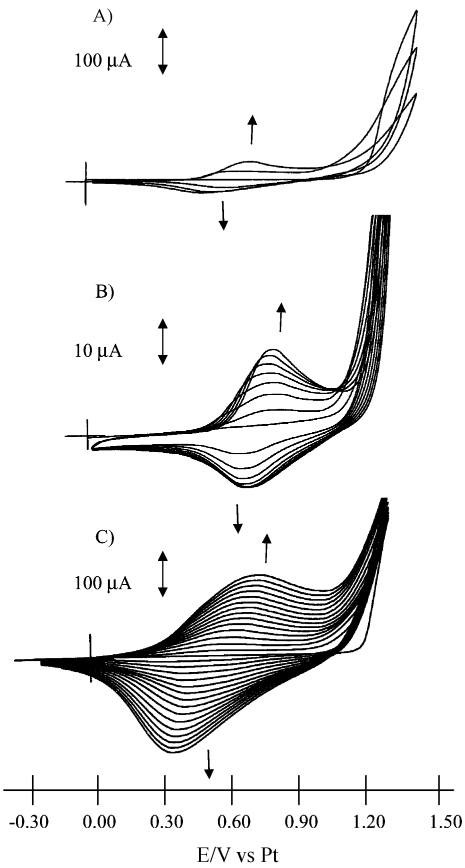

Fig. 5 Electrochemical copolymerisation of **1** and 3-MeT: consecutive cyclic voltammogramms: A) between 0 and 1.45 V, [**1**] = 6.9×10^{-2} M, [3-MeT] = 3×10^{-2} M, [3-MeT]/[**1**] = 0.435, scan rate: 200 mV s^{-1}; B) between 0 and 1.35 V, [**1**] = 1.25×10^{-2} M, [3-MeT] = 5×10^{-2} M, [3-MeT]/[**1**] = 4, scan rate: 500 mV s^{-1}; C) between 0 and 1.30 V, [**1**] = 8.0×10^{-2} M, [3-MeT] = 9.1×10^{-3} M, [3-MeT]/[**1**] = 8.78, scan rate: 200 mV s^{-1}. Electrolyte solution: CH_3CN + TBAP (0.1 M). The arrows indicate the direction of growth of the new wave.

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