JOURNAL OF Materials CHEMISTRY

Electrochemical molecular recognition of silver cation by electropolymerised thieno[3′,4′:5,6][1,4]dithiino[2,3-*b*]quinoxaline: a joint experimental and theoretical study

Leonid M. Goldenberg,†[a] Peter J. Skabara,*‡[b] Donna M. Roberts,[b] Rory Berridge,[b] Enrique Ortí,[c] Pedro M. Viruela[c] and Rosendo Pou-Amérigo[c]

[a]*Institute of Problems of Chemical Physics, Russian Academy of Science, Chernogolovka, Moscow region, Russia 142432*
[b]*Division of Chemistry, Sheffield Hallam University, Sheffield, UK S1 1WB. E-mail: peter.skabara@man.ac.uk*
[c]*Department of Physical Chemistry, University of Valencia, Valencia, Spain 46100*

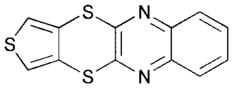
Received 16th May 2000, Accepted 21st July 2000
First published as an Advance Article on the web 21st September 2000

The novel annelated monomer thieno[3′,4′:5,6][1,4]dithiino[2,3-*b*]quinoxaline **1** has been electropolymerised on a variety of electrodes, resulting in films which are electroactive in non-aqueous and aqueous solution. The polymer films exhibit a transformation in voltammetric response corresponding to a positive shift in redox potential in the presence of silver cation, the maximum shift being *ca.* 150 mV in acetonitrile and *ca.* 400 mV in aqueous $LiClO_4$ solution. Mercury dication demonstrates a similar, but smaller (*ca.* 130 mV) shift in aqueous solution. Theoretical calculations clearly show the potential of poly(**1**) as a metal complexation agent. The Ag^+ ion coordinates with **1** in two ways: (i) an apical conformation involving the two dithiine sulfurs and (ii) a lateral σ-complex with a contribution from the quinoxaline nitrogens. The Hg^{2+} ion prefers to coordinate with the sulfur atoms. The calculations performed for the trimer illustrate that the metal ions can be coordinated simultaneously by two repeat units in the polymer chain.

Introduction

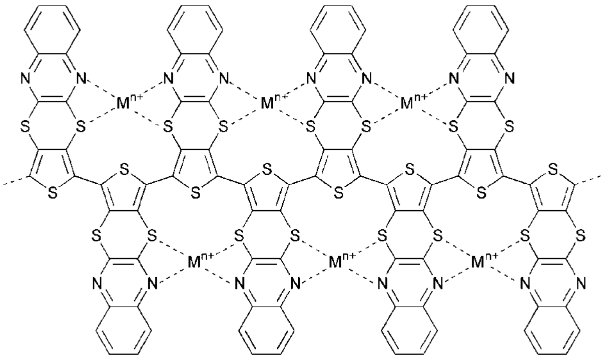
The study of redox-active receptor molecules, in which a change in the electrochemical behaviour of a signaling redox unit is used to monitor the complexation of neutral or ionic guest species, is an increasingly important area of supramolecular chemistry.[1] This type of molecular and ion recognition sensor is based on a host–guest arrangement involving the receptor molecule and the analyte. The application of this mechanism to thin solid films is particularly relevant for the construction of sensor devices.[2] In this context, the use of conjugated polymers is an important area of research[2,3] and considerable efforts have been directed towards the use of versatile polythiophene derivatives.[4] Amongst metal cations, alkali metals are typical analytical targets.[5] Recently, voltammetric Ag^+ recognition was observed with self-assembled monolayers of crown-annelated tetrathiafulvalenes.[6] To the best of our knowledge there are only a few known examples of the electrochemical recognition of transition metal ions with conjugated polymer films (*e.g.* complexation of macrocycles with transition metals was observed in the case of polypyrrole and polythiophene).[7]

In the preceding paper, we have reported the synthesis and electrochemical properties of a novel annelated thiophene derivative, thieno[3′,4′:5,6][1,4]dithiino[2,3-*b*]quinoxaline **1**.[8]



1

Compound **1** contains a quinoxaline moiety, possessing two sp^2 nitrogen atoms, which are potentially capable of coordinating to metal cations. The chelating ability of quinoxaline derivatives is well-founded and a number of quinoxaline-containing transition metal complexes have been reported in the literature;[9] hence, the propensity for poly(**1**) to bind to transition metals is fully justified. Furthermore, there is also a strong possibility of the interaction of metal cations with the two sulfur atoms in the dithiine ring, resulting in a complexed polymer material, such as that shown in the hypothetical fully saturated system **2**. Herein, we report on the interaction and electrochemical recognition of silver and mercury cations with electropolymerised films derived from monomer **1**.



2

Results and discussion

Compound **1** represents a thiophene derivative bearing sulfide groups; although these types of monomers can be difficult to polymerise electrochemically, there are several known examples of polythiophenes incorporating thioalkyl side groups.[10] The electrochemical behaviour of compound **1** has already

---

†Present address: Institute of Thin Film Technology and Microsensorics, Berlin, Germany.
‡Present address: Department of Chemistry, University of Manchester, Manchester, UK.

DOI: 10.1039/b003914o

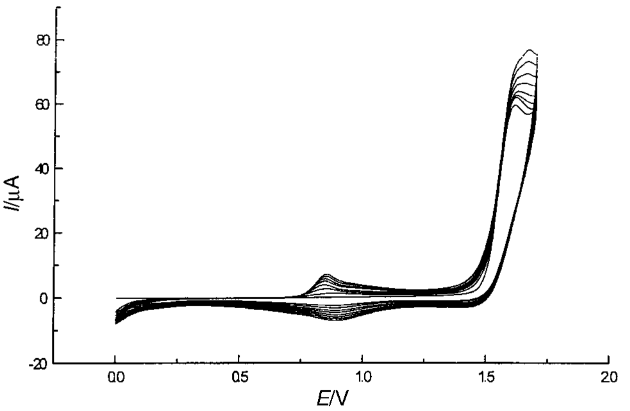


Fig. 1 CV of electropolymerisation of compound **1**, 10^{-3} M, in 0.1 M Bu_4NClO_4–CH_2Cl_2, scan rate 0.2 V s^{-1}, Au disk 1.6 mm diameter, *vs.* Ag/AgCl.

been reported,[8] however, continuous scanning over the first oxidation peak (from 0.0 to +1.7 V, *vs.* Ag/AgCl), leads to the polymerisation of **1**. The electropolymerisation of **1** was carried out using Pt, Au or glassy carbon (GC) electrodes in dry dichloromethane. The procedure resulted in the appearance of new redox couples at about 0.8 and 1.6 V *vs.* Ag/AgCl. Upon polymerisation, a yellow–brown film is visible at the Pt electrode. The typical voltammogram for electropolymerisation is represented in Fig. 1. The charge (Q) consumed under the first oxidation peak was determined by graphical integration. The growth of polymer redox peaks achieves saturation at Γ of *ca.* 4–5 nM cm^{-2}. The electropolymerisation process depended on the time at which the monomer solution was prepared; the first electropolymerisation from a fresh solution required a higher potential and proceeded more slowly. The shape of the polymer redox response (the ratio of currents for the first and second redox couples) depends on the nature of the electrode and the surface concentration(Γ). The resulting polymer films appear to be electroactive either in non-aqueous or aqueous electrolytes (Fig. 2), and the response proved to be relatively stable, *e.g.* in acetonitrile, the peak current decreases by only 5–10 % over 10 cycles at 0.05 V s^{-1}. Thicker films (with maximum Γ) on GC electrodes usually exhibit a CV response with a low undeveloped reduction peak, possibly due to hindered ion diffusion. In both water and acetonitrile, the peak current was proportional to the scan rate, which indicates a surface electrochemical reaction.

The interaction of several transition metal cations was investigated and, most notably, Ag^+ exhibited definitive indications of recognition behaviour. For different polymer films (different electrodes and Γ), addition of the Ag^+ cation led to a change of CV response, such that the oxidation peak potential (E_{pa}) or both oxidation (E_{pa}) and reduction (E_{pc}) peak potentials shifted positively. A change in the CV shape was also observed, *e.g.* with Au electrodes the electroactivity often increased after the first aliquot of Ag^+ was added. An example of the CV transformation upon addition of silver ion to the electrolyte solution is represented in Fig. 3. For some electrodes smaller, less positive oxidation peaks with a weaker sensitivity to Ag^+ were observed in the CV response. This may be due to the existence of domains with different properties in the polymer film. The response to Ag^+ starts at the concentration level of 10^{-4} M and saturates at about 10^{-2} M with a maximum shift up to *ca.* 150 mV. The level of reproducibility obtained with different electrodes (Au or GC), counteranions (from $AgClO_4$, $AgBF_4$ or $AgNO_3$) and methods (Ag/AgCl or ferrocene internal reference) to determine the potential shift was found to be high.

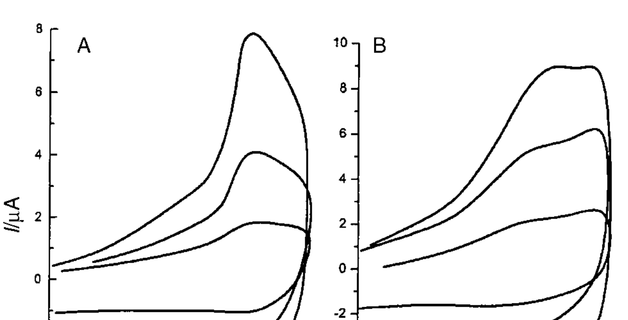


Fig. 2 CV response of poly(**1**) electrode, GC, *vs.* Ag/AgCl: (A) (Γ=1.1 nM cm^{-2}), 0.2 M Bu_4NClO_4–CH_3CN, scan rate 0.02, 0.05 and 0.1 V s^{-1}, respectively; (B) (Γ=1.3 nM cm^{-2}), 0.1 M H_2SO_4, scan rate 0.05, 0.1 and 0.2 V s^{-1}, respectively.

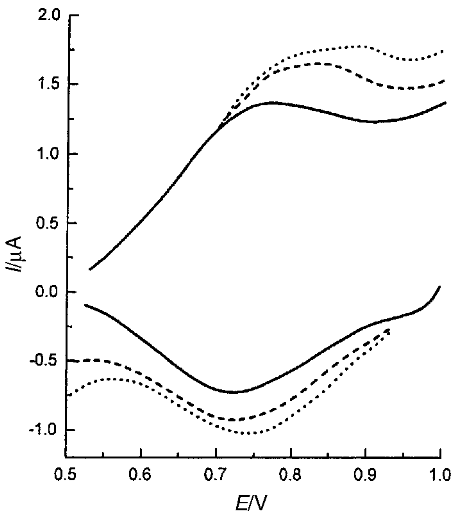


Fig. 3 CV response of poly(**1**) electrode in 0.2 M $LiClO_4$–CH_3CN at Au electrode (Γ=2.3 nM cm^{-2}), scan rate 0.05 V s^{-1}, *vs.* Ag/AgCl, second scan shown (—), $AgNO_3$ used: 1.7×10^{-3} M of Ag^+ (---), 1.3×10^{-2} M of Ag^+ (···).

We have previously used a simplified approach to estimate the binding constant for voltammetric cation recognition in solution by a redox active host.[6,11] This assumes that the concentration of the complex is related to the voltammetric potential. Alternatively, to treat data for spectroscopic titration the simple equation (1) is often used:[12]

$$(A_0-A)/(A-A_i)=K[M^+] \tag{1}$$

where A is the absorbance, A_0 is the absorbance at zero concentration of M^+ and A_i is the absorbance at an infinite (or saturated) M^+ concentration.

Substitution of the absorbance for the potential in equation (1) results in equation (2):

$$K[M^+]=(E_0-E)/(E-E_i) \tag{2}$$

or in terms of potential shift equation (3):

$$K[M^+]=(-\Delta E)/(\Delta E-\Delta E_i) \tag{3}$$

where ΔE_i is the maximum shift at an infinite M^+ concentration. Applying non-linear fitting to the dependence of ΔE *vs.* $[M^+]$ we obtain an estimate of K and ΔE_i. A typical fit is shown in Fig. 4 and the results are collated in Table 1. We should note that another approach used for solution electrochemical complexation[13] does not give the expected linear relation, and so cannot be used in this case.

The change of CV response in acidic solution (HBF_4) was

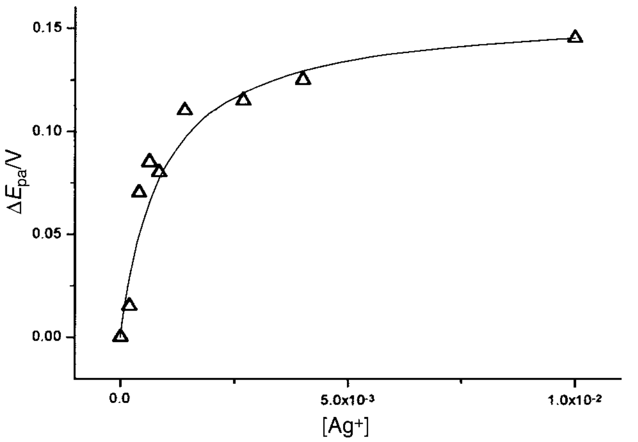


Fig. 4 Fit of CV data to equation (3);0.2 M $LiClO_4$–CH_3CN *vs.* [Ag^+] (Δ), $\Delta E_i = 158 \pm 2$ mV, $K = 1102 \pm 140$.

either not observed or small (with a shift of E_{pc} *ca.* 20 mV), possibly due to protonation of the quinoxaline unit (in general, 5,6-disubstituted-1,4-dithiino[2,3-*b*]quinoxaline derivatives can be efficiently alkylated or protonated at the sp^2 nitrogen atoms of the quinoxaline unit to give the corresponding salts).[14] Therefore, we used a neutral aqueous electrolyte even though the electroactivity in the neutral solution was lower. A relatively well pronounced CV response was observed on GC electrode (due to lower background current). These films demonstrated a response to Ag^+ cation (Fig. 5) with the maximum shift of E_{pc} being up to *ca.* 400 mV. The dependence of peak shift *versus* concentration of silver cation is shown in Fig. 6, which demonstrates the possibility of detection at a 10^{-5} M level. The binding of silver cations by the polymer film appears to be reversible. The original peak position can be predominantly restored by soaking the electrode in KCl solution for half an hour (the bound silver cation is expelled as insoluble AgCl). On the contrary, soaking the electrode in water, even for 20 h, results in only a slight restoration of E_{pc}. Application of the aforementioned non-linear fitting procedure to the data-sets obtained in aqueous solution results in higher values of log$K$ and ΔE_i (Table 1) than in acetonitrile. This may indicate stronger binding of the soft silver cation in a hard solvent (*i.e.* water); a similar phenomenon was observed in binding Ag^+ to crown-annelated tetrathiafulvalene.[6]

In aqueous solution, we were able to demonstrate the principal possibility of amperometric Ag^+ detection (Fig. 7) by application of a series of short (1 s) pulses, from the region where the polymer is in the neutral state to the potential of E_{pa}.

As an independent test in both aqueous and acetonitrile electrolytes, using similar experimental parameters (or exactly in the same solution in parallel with poly(**1**) electrodes) we have run the Pt electrodes modified with films of polymethylthiophene (PMT) obtained by electropolymerisation under similar conditions. No definitive response for Ag^+ was observed for PMT electrodes.

Table 1 Voltammetric recognition parameters for different cations

Cation; conditions	ΔE / mV	logK^d	ΔE_i / mV^d
Ag^+; acetonitrile	150	2.1–3.2	110–180
Ag^+; HBF_4	0		
Ag^+; $LiClO_4$ aqueous	400^a	3.9–4.5	240–420
Hg^{2+}; acetonitrile	30^b		
Hg^{2+}; $LiClO_4$ aqueous	130^a	2.7–2.8	100–175
Ni^{2+}; acetonitrile	−30^c		

$^a\Delta E_{pc}$. ^{b}A small shift was observed with $Hg(NO_3)_2nH_2O$, but not with $HgCl_2$. $Hg(NO_3)_2nH_2O$ is only slightly soluble in acetonitrile and maximum concentration was estimated to be *ca.* 5×10^{-4}–1×10^{-3} M. The issue is also complicated by the reduction of Hg^{2+} occurring at the beginning of polymer wave. $^c\Delta E_{pa}$. ^{d}Non-linear fit to equation (3)

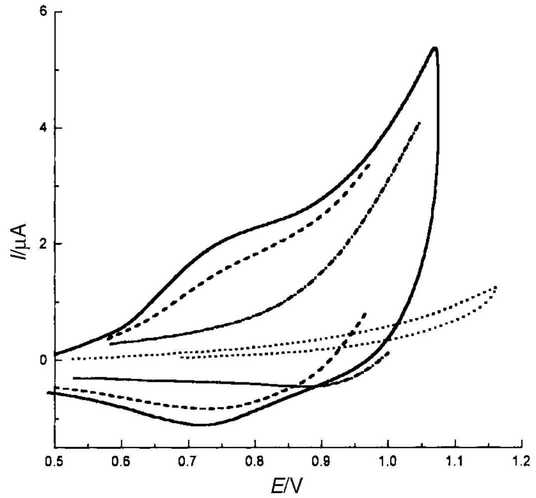


Fig. 5 CV response of poly(**1**)/GC electrode ($\Gamma = 2.1$ nM cm^{-2}) in 0.5 M aqueous $LiClO_4$, scan rate 0.02 V s^{-1}, $AgClO_4nH_2O$ used: blank electrode (···); polymer (—); polymer with 1.8×10^{-5} M of Ag^+ (---); polymer with 1×10^{-4} M of Ag^+ (— — —).

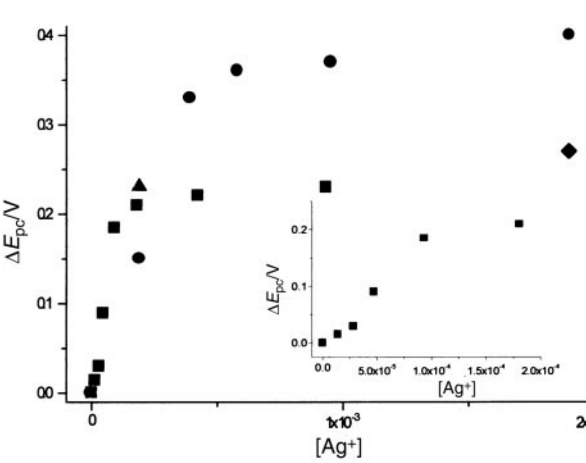


Fig. 6 The shift of poly(**1**)/Au electrode reduction potential (E_{pc}) in 0.5 M aqueous $LiClO_4$ *versus* [Ag^+]: $\Gamma = 1.7$ (■), 2.3 (●), 1.4 (▲) and 2.0 nM cm^{-2} (◆), respectively. Insert shows extended scale for (■).

Similar results were observed in aqueous solution for the soft dication Hg^{2+} however, the effect was weaker than for Ag^+ (Table 1). Correspondingly, only a slight response has been registered for mercury in acetonitrile.

A small but negative shift was also observed at a low concentration (*ca.* 8×10^{-5} M) of Ni^{2+} cations (data not shown) in acetonitrile containing 0.2% water (to suppress the influence of water from $Ni(NO_3)_2 \times 6H_2O$, which seems to have an opposite effect). Following this, the CV was stable even at a much higher concentration of Ni^{2+}. We were not able to prove unambiguously such a shift in aqueous media, because the CV in aqueous electrolyte was less resolved.

Theoretical calculations

The metal-complexation abilities of poly(**1**) were investigated theoretically by calculating the interaction of Ag^+ and Hg^{2+} metal ions with compound **1** and its trimer. For metal ion-molecule complexes, it has been shown that systems with essentially electrostatic interactions can be well described at the Hartree–Fock (HF) level.[15,16] Electron correlation effects need, however, to be included to account for possible electron donation between transition metals and the ligand. Calculations were thus performed within the density functional theory

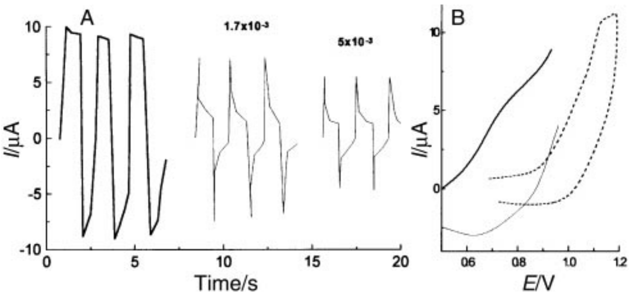


Fig. 7 (A) Current–time response for poly(**1**)/GC electrode ($\Gamma = 3.9$ nM cm^{-2}) in 0.5 M aqueous $LiClO_4$ on application of a sequence of three potential pulses 0.5→0.8 V *vs.* Ag/AgCl, duration 1 sc; [Ag$^+$] are indicated. (B) Initial CV and CV after completion of experiment, *vs.* Ag/AgCl.

(DFT) using the hybrid B3P86 functional and the 6-31G* (C, N, S, O and H atoms) and LANL2DZ (Ag and Hg atoms) basis sets. The DFT approach includes electron correlation effects at a relatively low computer cost and has been shown to provide geometries and binding energies in good agreement with experimental results and with more elaborated MP2 and CCSD(T) calculations for the Ag$^+$–pyridine and Ag$^+$–benzene complexes.[17,18]

M^{n+}-Monomer (1). As discussed in the preceding paper,[8] compound **1** presents a nonplanar C_s structure folded along the axis defined by the sulfur atoms of the dithiine ring. The coordination sites of the Ag$^+$ ion were first explored within C_s symmetry constraints. The metal atom was placed in different positions along the symmetry plane bisecting the molecule and the geometry of the complex was fully relaxed. Four different C_s structures were thus converged for the Ag$^+$-complex. The most stable corresponds to the apical system depicted in Fig. 8a, in which the Ag$^+$ ion is centred above the sulfur atoms. This conformation was achieved by calculation after positioning the Ag$^+$ ion over the dithiine ring and also when it was initially located over the pyrazine ring of the quinoxaline moiety. The Ag$^+$ ion does not coordinate with the π-system of the pyrazine ring and migrates to the dithiine ring. The same result was obtained when the Ag$^+$ ion was moved along the N···N axis, thus breaking the C_s symmetry. The Ag$^+$ ion was afterwards placed under the plane of the molecule centred below the dithiine ring and below the pyrazine ring. In the first case, the optimisation ended up with the Ag$^+$ ion interacting with the C–C bond fusing the thiophene and dithiine rings (Ag–C: 2.513 Å). In the second case, the Ag$^+$ ion migrates to the outermost C–C bond of the quinoxaline moiety (Ag–C: 2.397 Å). The optimised structures are 19.90 and 15.52 kcal mol^{-1} higher in energy than the apical coordination shown in Fig. 8a. The fourth C_s structure was obtained by placing the Ag$^+$ ion in front of the thiophene sulfur, eliciting a σ-type complex. However, the ion did not remain in the plane of the thiophene unit and migrated above the ring, forming an angle of 72.2° (Ag–S: 2.500 Å). The resulting structure is 19.17 kcal mol^{-1} higher in energy than the apical complex.

In a similar study, we considered the σ interaction of the Ag$^+$ ion with the sulfur and nitrogen atoms of the dithiine and pyrazine rings. The ion was initially placed midway between these atoms in the plane of the quinoxaline ring. Optimisation led to the complex depicted in Fig. 8b, in which the Ag$^+$ ion stays in the quinoxaline plane and is mainly coordinated to the nitrogen atom. This structure competes in stability with the C_s structure shown in Fig. 8a since it is only 1.75 kcal mol^{-1} higher in energy.

Two energetically-favoured coordination structures are therefore obtained for the Ag$^+$–**1** complex: the apical C_s structure involving the dithiine sulfurs (hereafter named *the apical complex*) and the nonsymmetric σ structure involving both the nitrogen and sulfur atoms (hereafter named *the lateral complex*). The discussion presented below focuses on these two structures. The other three coordination sites found are energetically less favoured and are highly unlikely to occur in the electrochemical solution where the Ag$^+$ ions are surrounded by solvent molecules and are interacting with their counterions.

The molecular structure of compound **1** in the apical complex is almost identical to that observed for the isolated molecule,[8] the main changes being detected for the dithiine moiety. Due to the interaction with the Ag$^+$ ion, the S–C bond distances lengthen from 1.761 and 1.775 Å in **1** to 1.771 and 1.803 Å in the apical complex, and the folding of the dithiine ring along the S···S axis increases from 42.3° to 55.6°. For the lateral complex, the geometry of **1** undergoes even smaller changes and the dithiine ring is folded by 46.5°. The Ag–S distances in the apical complex are calculated to be 2.659 Å. These distances are in good agreement with those observed experimentally for Ag$^+$ complexes with sulfur-containing compounds such as heterocyclic thiones (2.67 Å)[19] or dialkyl thioethers (2.67 Å).[20] For the lateral complex, the Ag$^+$ ion lies at a distance of 2.900 Å from the sulfur atom and 2.242 Å from the nitrogen atom. These distances suggest that interaction takes place only with the nitrogen atom, but some interaction with sulfur is also detected because: (i) the Ag$^+$ ion is not on the N···N axis and (ii) the Ag–N distance is longer than that found in the Ag$^+$–pyridine complex using a similar functional approach (2.190 Å).[17]

The binding energies calculated at the B3P86/6–31G* level for the apical and lateral Ag$^+$–**1** complexes are 57.2 and 55.4 kcal mol^{-1}, respectively.[21] These energies are larger than those reported for the Ag$^+$–pyridine σ-complex (experimental: 45.2 kcal mol^{-1}; theoretical (B3LYP): 42.5 kcal mol^{-1})[17] and those observed for the Ag$^+$–benzene π-complex (35.5 kcal 14;mol^{-1}).[22,23]

Natural bond orbital (NBO) analysis was performed on the apical and lateral complexes. The charges on the Ag$^+$ cation are +0.74 e and +0.82 e, respectively. These charges suggest a noticeable electron transfer from molecule **1** to the Ag$^+$ cation in both the apical (0.26 e) and lateral (0.18 e) complexes. The electrons transferred go to the valence 5s orbital of Ag$^+$ (4d^{10}5s^0), which shows an occupancy of 0.27 e and 0.20 e in the apical and lateral complexes, respectively.

Fig. 9 sketches the atomic orbital (AO) composition of the highest occupied molecular orbital (HOMO) of the Ag$^+$–**1**

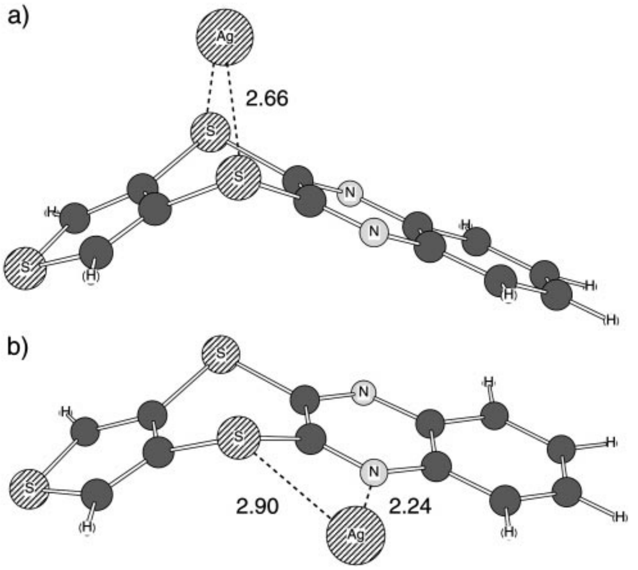


Fig. 8 B3P86-optimised structures calculated for the Ag$^+$–**1** complex: (a) apical complex (C_s symmetry) and (b) lateral complex. Distances are given in Å.

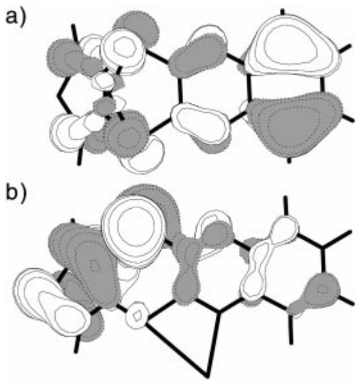


Fig. 9 Electron density contours calculated for the HOMO of the Ag^+–**1** complex: (a) apical complex (C_s symmetry) and (b) lateral complex.

complex for both the apical and lateral structures. While the HOMO of the apical complex is largely located on the quinoxaline moiety, the HOMO of the lateral complex mainly spreads over the thiophene and dithiine rings. In both cases the contribution of the Ag^+ ion is negligible. These topologies suggest that when the complex is oxidised, the electron is extracted from different regions of the molecule depending on the structure of the complex. Since the energy of the HOMO is higher for the lateral complex (−9.91 eV) than for the apical complex (−10.51 eV), the former can be expected to oxidise more easily.

To get a deeper insight into the oxidation process, the oxidised forms of the Ag^+–**1** complexes (*i.e.*, the $[Ag^+–\mathbf{1}]^{+\bullet}$ open-shell dicationic species) were optimised. For the apical complex, the oxidised form preserves the folded structure shown in Fig. 8a because, as suggested by the AO composition of the HOMO, the electron is mainly extracted from the quinoxaline moiety (quinoxaline: 0.83 e, dithiine sulfurs: 0.11 e, Ag^+: 0.06 e). The oxidised form of the lateral complex is by contrast almost planar (average folding angle: 8.4°) because the electron is now mainly removed from the dithiine sulfurs (0.48 e) and from the thiophene ring (0.28 e). The oxidation process is, in this case, similar to that undergone by the isolated molecule **1**[8] and implies the partial aromatisation of the dithiine ring. The Ag^+ ion now lies on the N···N axis and is only coordinated to the nitrogen atom. As suggested by the HOMO energies, the energy required to oxidise the apical complex (11.91 eV) is larger than that needed to remove an electron from the lateral complex (11.12 eV).

The coordination of Hg^{2+} to **1** was investigated starting from the structures calculated for the apical and lateral complexes of Ag^+. After optimising the geometry, the apical complex preserves the structure depicted in Fig. 8a for the Ag^+ complex but now the Hg^{2+} ion is at a coordination distance of 3.023 Å from the sulfur atoms. For the lateral complex, the Hg^{2+} ion does not maintain σ-coordination to the nitrogen atom and migrates to a lateral position 2.7 Å over the molecular plane at a distance of 3.199 Å from one of the dithiine sulfurs. This structure is 2.81 kcal mol^{-1} higher in energy than the apical complex and the dithiinoquinoxaline moiety is fully planar.

As expected, the binding energies calculated for the Hg^{2+}–**1** complex (201.6 kcal mol^{-1} for the apical structure) are higher than those obtained for the Ag^+–**1** complex due to the larger charge of the Hg^{2+} ion. The NBO analysis indicates that a very large electron transfer, greater than one electron, takes place from molecule **1** to the valence 6s orbital of the Hg^{2+} ($5d^{10}6s^0$) ion, which exhibits net atomic charges of only +0.75 e (apical complex) and +0.50 e (lateral complex). The occupancies calculated for the 6s orbital are 1.24 e and 1.50 e, respectively, while no $6d(Hg^{2+})\rightarrow\pi^*(\mathbf{1})$ electron transfer is detected. For the lateral complex, 0.67 e are transferred from the dithiine sulfurs, thereby explaining the planarisation of the ligand by the aromatisation of the dithiine ring. The S–C bond distances (1.72–1.74 Å) are indeed similar to those obtained for $\mathbf{1}^{+\bullet}$ (1.73–1.74 Å).

The $[Hg^{2+}–\mathbf{1}]^{+\bullet}$ trication was also calculated to simulate the oxidation of the complex. For the apical form, the complex preserves its structure because the electron is mainly extracted from the quinoxaline moiety as in the Ag^+–**1** complex. For the lateral complex, the electron is mainly obtained from the dithiine ring and the complex breaks down (the Hg atom moves away) due to the large charge accumulated by the sulfur atoms.

Theoretical calculations clearly suggest that both the Ag^+ and Hg^{2+} ions coordinate to molecule **1**, the apical coordination with the dithiine sulfurs being slightly favoured. The theoretical results should be taken with caution, however, since they have been obtained in the gas phase. In the electrochemical solution the scene is much more complex since the metal ions are interacting with their counterions and are surrounded by the molecules of the solvent.

To investigate the effect of the counterions, we reoptimised the apical structure of the Ag^+–**1** and Hg^{2+}–**1** complexes including NO_3^- anions (see Fig. 10). The presence of the NO_3^- counterions does not modify the structure of the complexes but drastically reduces the binding energies of the metal to molecule **1**.[21] For the Ag^+–**1** complex, the value calculated for the binding energy is now 22.6 kcal mol^{-1}, compared to the value of 57.2 kcal mol^{-1} obtained in the absence of the counterion. For the Hg^{2+}–**1** complex, the metal coordination to the molecule is maintained by a binding energy of only 13.2 kcal mol^{-1} in the presence of the counterions (201.6 kcal mol^{-1} in their absence). The electron transfer from **1** to the metal ion is also reduced, especially for the Hg^{2+} complex, and has similar values to the Ag^+ (0.11 e) and Hg^{2+} (0.13 e) complexes.

Our theoretical calculations indicate that, in the presence of metal counterions, the Hg^{2+}–**1** complex is weaker than the Ag^+–**1** complex. This result is in agreement with the smaller shifts detected in the oxidation potential of poly(**1**) in the

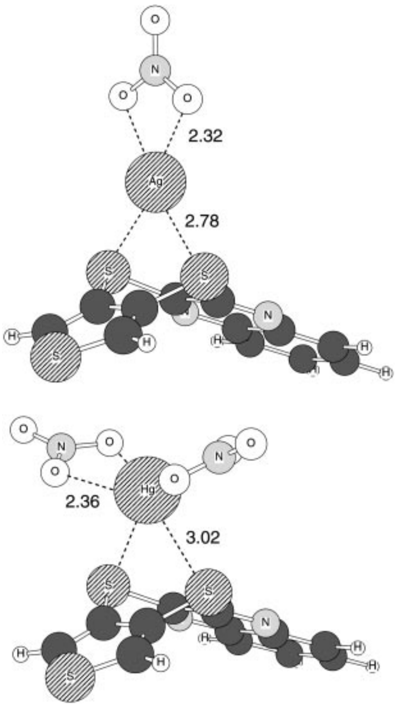


Fig. 10 B3P86-optimised structures calculated for apical Ag^+–**1** (top) and Hg^{2+}–**1** (bottom) complexes in the presence of NO_3^- counterions. Both structures have C_s symmetry. Selected bond distances are given in Å.

presence of mercury dication (particularly in acetonitrile solution). In aqueous solution, the Ag^+ and Hg^{2+} ions are solvated by water molecules, reducing the interaction with the counterions; however, this solvation effect can also disrupt the chelating effect of the polymer.

M^{n+}-Trimer. In order to study the coordination of Ag^+ and Hg^{2+} to poly(**1**), the interaction of these ions with a trimer of **1** was investigated. Firstly, the molecular structure of the trimer was fully optimised at the B3P86/6–31G* level. As depicted in Fig. 11, two minimum-energy conformations, *A* and *B*, were found for the trimer. Conformation *A* corresponds to a right-handed helical structure in which each thiophene ring is twisted by *ca.* 114° around the interannular α–α′ bonds. Conformation *B* corresponds to a zigzag structure in which thiophene rings are twisted alternately clockwise and counter-clockwise by 107° and 122°. The degree of twisting from the all-*anti* conformation (180°) is higher than that found for unsubstituted α,α′-oligothiophenes[24–26] owing to the interaction between the sulfur atoms of the dithiine and thiophene rings on adjacent units. For a fully planar *anti* conformation, the distance between those atoms is only 2.8 Å. For the fully relaxed conformations *A* and *B*, the S(dithiine)···S(thiophene) distances are in the range 3.6–3.8 Å which embody the value of the van der Waals S···S distance (3.70 Å).[27] Conformations *A* and *B* are almost isoenergetic, the helical conformation being the most stable by only 0.47 kcal mol^{-1}.

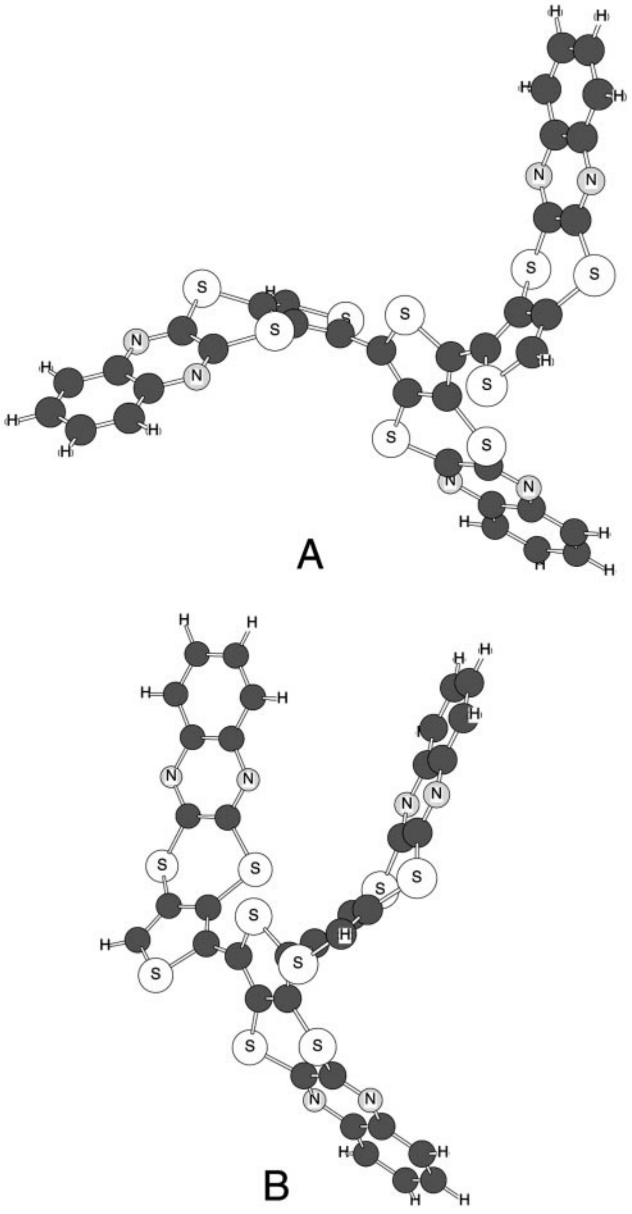


Fig. 11 B3P86-optimised minimum-energy conformations *A* and *B* calculated for the trimer of **1**.

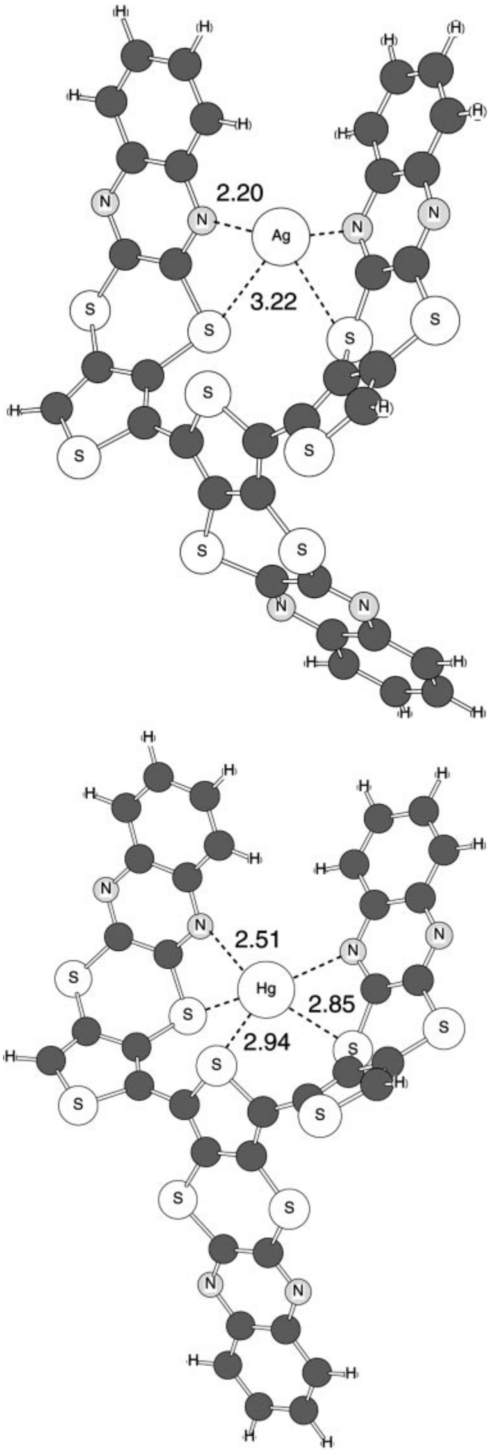


Fig. 12 B3P86-optimised structures calculated for the trimer of **1** coordinated with Ag^+ (upper) and Hg^{2+} (lower). Selected bond distances are given in Å.

The conformations calculated for the trimer can be used as patterns to build up the polymer chains. Conformation *A* leads to a wide-open helical structure through which metal ions can easily diffuse and coordinate to the dithiinoquinoxaline moieties forming the apical and lateral complexes discussed above. Conformation *B* would lead, by contrast, to a more compact structure in which monomeric units lie approximately in the same plane. This structure opens the possibility that metal ions coordinate simultaneously to two adjacent dithiinoquinoxaline units as suggested in **2**. We studied this possibility by optimising the *B* conformation of the trimer including a silver cation or a mercury dication between the external units. Fig. 12 sketches the structures found for both complexes. The Ag^+ ion moves away from the sulfur atoms and coordinates to the quinoxaline nitrogens (Ag–N: 2.20 Å). The complex formed has a binding energy of 93.8 kcal mol^{-1}. This energy is greater than that found for the lateral Ag^+–**1** complex (55.4 kcal mol^{-1}) because the Ag^+ ion is now σ-coordinated to two nitrogens. The Hg^{2+} ion prefers to stay centred among the heteroatoms and is coordinated to the quinoxaline nitrogens (Hg–N: 2.51 and 2.52 Å), to the dithiine sulfurs (Hg–S: 2.83 and 2.86 Å) and to the thiophene sulfur (Hg–S: 2.94 Å). It is to be stressed that the structure of the trimer is largely distorted to allow the coordination of the Hg^{2+} ion. By contrast, the inclusion of the Ag^+ ion does not significantly change the structure and conformation of the trimer. This means that the coordination of the Hg^{2+} ion may be restricted by the rigidity of the polymer. Again, the molecules of the solvent and the counterions will play an important role in the coordination process because they also diffuse into the polymer film.

Conclusions

The novel annelated thiophene monomer thieno[3′,4′:5,6][1,4]-dithiino[2,3-*b*]quinoxaline **1** has been electropolymerised on different types of electrode, affording polymer films which are electroactive in non-aqueous and aqueous media. In the presence of silver cation, poly(**1**) demonstrates an increase in redox potential, with the maximum shift in acetonitrile being *ca.* 150 mV. Stronger binding of this soft cation was observed in aqueous $LiClO_4$ solution, the maximum shift being *ca.* 400 mV. Mercury dication also exhibits a shift of *ca.* 130 mV in the E_{pa} of poly(**1**) in neutral aqueous solution.

B3P86 calculations show that both the silver cation and the mercury dication coordinate to monomer **1**. The calculations predict an apical coordination involving the dithiine sulfurs as the favoured chelating atoms. σ-Coordination to the quinoxaline nitrogens also takes place for the Ag^+ ion with a similar binding energy. In the presence of NO_3^- counterions, the binding energies of the Ag^+–**1** and Hg^{2+}–**1** complexes are drastically reduced and the Ag^+–**1** complex is calculated to be more stable. The minimum-energy conformations obtained for the trimer of **1** show that the polymer can incorporate the metal ions coordinated to two adjacent dithiinoquinoxaline units as suggested in **2**.

The results here show a new type of conjugated polymer system, showing the rare ability of sensing transition metal ions in solution.

Experimental

A PI-50 potentiostat with a PR-8 programmer and an LKD-4 X-Y recorder (all Russian) were used for electrochemical experiments. A Pt wire served as the counter electrode and a Pt or Au disk electrode (1.6 mm diameter), or glassy carbon (GC) disk electrode (3 mm diameter, all BAS) as the working electrode. Ag/Ag^+ or Ag/AgCl/KCl (sat) were used as the reference electrodes. To avoid deposition of AgCl in the experiments with Ag^+, the latter electrode was separated from the cell solution by a junction with graphite sealed in glass. Ferrocene was also used as the internal reference in recognition studies in acetonitrile and potentials were quoted *versus* Fc/Fc^+, measured on a bare Pt electrode. However, the former reference electrode (Ag/AgCl with a graphite second compartment) proved to be more stable and allowed us to observe the potential shift upon addition of Ag^+. Metal cations were introduced into the cell as concentrated solutions in the same solvent or as solid aliquots.

The synthesis of compound **1** has been described previously.[8] Methylthiophene (Aldrich) was used for electropolymerisation as received. Acetonitrile was heated under reflux with $KMnO_4 + Na_2CO_3$, distilled, treated with H_2SO_4, and distilled for a second time over P_2O_5; dichloromethane was treated in turn with concentrated H_2SO_4, $NaHCO_3$ solution and water, dried over $CaCl_2$, and distilled twice over P_2O_5. Bu_4NClO_4 (Fluka, electrochemical grade), $LiClO_4$ (Fluka, microselect), H_2SO_4, HBF_4 (prepared from B_2O_3 and hydrofluoric acid), were used for the preparation of electrolyte solutions. $AgBF_4$, $AgClO_4nH_2O$, $Hg(NO_3)_2nH_2O$ (all Aldrich), $AgNO_3$ (pure, Russian manufacture, or Fluka puriss.), $Ni(NO_3)_2n6H_2O$ (pure for analysis), $AgClO_3$, $HgCl_2$ (both pure, Russian manufacture) were used for aliquots of transition metal cations.

Computational details

All the calculations were performed using the hybrid, gradient-corrected B3P86 density functional[28] and the Gaussian 98 software package.[29] The split-valence, double-ζ 6–31G* basis set[30] was used for C, N, O, S and H atoms and the double-ζ valence LANL2DZ basis set[31] for Ag and Hg atoms. The LANL2DZ basis set incorporates quasirelativistic effective core potentials (ECPs). Ag^+ and Hg^{2+} complexes are closed-shell systems and were computed using the restricted Hartree–Fock (RHF) formalism. The spin-unrestricted Hartree–Fock (UHF)[32] approximation was used to calculate the singly-oxidised forms of those complexes. No significant spin contamination was obtained for open-shell systems. The Berny analytical method[33] with standard threshold values for the maximum force (0.00045 arbitrary units) and maximum displacement (0.0018 arbitrary units) was employed for the optimisations. The optimisations of the trimer involve around 800 basis functions and were performed with no symmetry restriction. The first optimisation took approximately 10 days on a SGI origin 2000-R12000 computer running simultaneously on four CPUs. Atomic charges and atomic orbital populations were calculated using the natural population analysis (NPA) included in the natural bond orbital (NBO) scheme proposed by Weinhold and coworkers.[34] Three dimensional MO plots were generated with the 3.6 version of the MOLDEN program[35] using 0.03 contours.

Acknowledgements

LMG would like to thank the Russian Foundation for Basic Research (project 97-03-32268) for financial support. The group from Valencia gratefully acknowledges financial support from Spanish DGES-MEC under grants PB95-0428-C02-02, PB98-1447 and 1FD97-1765-C03-01.

References

1 P. D. Beer in *Transition Metals in Supramolecular Chemistry*, Eds. L. Fabbrizzi and A. Poggi, Kluwer Academic Publishers, Dordrecht, 1994, 33; P. D. Beer in *Advances in Inorganic Chemistry*, Academic Press, Inc., 1992, **39**, 79; P. D. Beer in *Molecular Engineering for Advanced Materials*, Eds. J. Becher and K. Schaumburg, Kluwer Academic Publishers, Dordrecht, 1995, 99;; P. D. Beer, *Acc. Chem. Res.*, 1998, **31**, 71.

2 L. M. Goldenberg, M. R. Bryce and M. C. Petty, *J. Mater. Chem.*, 1999, **9**, 1957.

3 T. M. Swager and M. J. Marsella, *Adv. Mater.*, 1994, **6**, 595; S. J. Higgins, *Chem. Soc. Rev.*, 1997, **26**, 247.

4 (*a*) M. Leclerc and K. Faïd, *Adv. Mater.*, 1994, **6**, 595; (*b*) R. D. McCullough, *Adv. Mater.*, 1998, **10**, 93; (*c*) J. Roncali in *Handbook of Conducting Polymers*, Eds. T. A. Skotheim, R. L. Elsenbaumer and J. R. Reynolds, Marcel Dekker, New York, 1998, 311; (*d*) J. Roncali, *J. Mater. Chem.*, 1999, **9**, 1875.

5 (*a*) J. Roncali, L. H. Shi and F. Garnier, *J. Phys. Chem.*, 1991, **95**,

8983; (*b*) H. Korri Youssoufi, M. Hmyene, F. Garnier and D. Delabouglise, *J. Chem. Soc., Chem. Commun.*, 1993, 1550; (*c*) H. Korri Youssoufi, P. Godillot, P. Srivastava, A. El Kassimi and F. Garnier, *Synth. Met.*, 1997, **84**, 169; (*d*) H. Korri Youssoufi, A. Yassar, S. Baiteche, M. Hmyene and F. Garnier, *Synth. Met.*, 1994, **67**, 251; (*e*) P. Bäuerle and S. Scheib, *Acta Polym.*, 1995, **46**, 124; (*f*) P. Bäuerle and S. Scheib, *Adv. Mater.*, 1993, **5**, 849; (*g*) M. J. Marsella, R. J. Newland, P. J. Carroll and T. M. Swager, *J. Am. Chem. Soc.*, 1995, **117**, 9842; (*h*) L. M. Goldenberg, I. Levesque, M. Leclerc and M. C. Petty, *J. Electroanal. Chem.*, 1998, **447**, 1; (*i*) L. M. Goldenberg, *Russ. Chem. Rev.*, 1997, **66**, 1033; (*j*) J. L. Reddinger and J. R. Reynolds, *Chem. Mater.*, 1998, **10**, 3.

6 A. J. Moore, L. M. Goldenberg, M. R. Bryce, M. C. Petty, A. P. Monkman, C. Morenco, J. Yarwood, M. J. Joyce and S. N. Port, *Adv. Mater.*, 1998, **10**, 395; M. R. Bryce, A. S. Batsanov, T. Finn, J. A. K. Howard, M. Kamenjicki, I. K. Lednev and S. A. Asher, *Chem. Commun.*, 2000, 295; *Br. Pat.* Application Number 9712694.0. International Patent Number WO98/58246, International Publication Date 23 December 1998.

7 (*a*) I. Tanigushi, K. Matsushita, M. Okamoto, J. L. Collin and J. P. Sauvage, *J. Electroanal. Chem.*, 1990, **280**, 221; (*b*) H. Korri Youssouffi, M. Hmyene, A. Yassar and F. Garnier, *J. Electroanal. Chem.*, 1996, **406**, 187.

8 See preceding paper; P. J. Skabara, R. Berridge, K. Prescott, L. M. Goldenberg, E. Ortí, R. Viruela, R. Pou-Amérigo, A. S. Batsanov, J. A K Howard, S. J. Coles and M. B. Hursthouse, *J. Mater. Chem.*, 2000, DOI: 10.1039/b003910l.

9 For example see: W. J. Geary, *J. Chem. Soc. A*, 1969, 71; W. J. Geary, *J. Chem. Soc. A*, 1969, 2118; D. F. Colton and W. J. Geary, *J. Chem. Soc. A*, 1971, 2457; D. F. Colton and W. J. Geary, *J. Chem. Soc., Dalton Trans.*, 1972, 547; D. F. Colton and W. J. Geary, *J. Inorg. Nucl. Chem.*, 1974, **36**, 1499.

10 G. Gourillon and F. Garnier, *J. Electroanal. Chem.*, 1984, **161**, 51; R. L. Elsenbaumer, K. Y. Jen and R. Oobodi, *Synth. Met.*, 1986, **15**, 169; S. Tanaka, M. Sato and K. Kaeriyama, *Synth. Met.*, 1988, **25**, 277; J. P. Ruiz, K. Nayak, D. S. Marynick and J. R. Reynolds, *Macromolecules*, 1989, **22**, 1231; C. Wang, J. L. Schindler, C. R. Kannewurf and M. G. Kanatzidis, *Chem. Mater.*, 1995, **7**, 58.

11 R. Dieing, V. Morisson, A. J. Moore, L. M. Goldenberg, M. R. Bryce, J.-M. Raoul, M. C. Petty, J. Garin, M. Saviron, I. K. Lednev, R. E. Hester and J. N. Moore, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1587.

12 I. K. Lednev and M. C. Petty, *Adv. Mater. Opt. Electron.*, 1995, **5**, 137; I. K. Lednev and M. C. Petty, *J. Phys. Chem.*, 1995, **99**, 4176.

13 R. R. Gagne, J. L. Allison and D. M. Ingle, *Inorg. Chem.*, 1979, **18**, 2767.

14 P. J. Skabara, unpublished results.

15 C. W. Bauschlicher and H. Partridge, *Chem. Phys. Lett.*, 1991, **181**, 129.

16 W. Lu and S. Yang, *J. Phys. Chem. A*, 1998, **102**, 825.

17 Y.-S. Yang, W.-Y. Hsu, H.-F. Lee, Y.-C. Huang, C.-S. Yeh and C.-H. Hu, *J. Phys. Chem. A*, 1999, **103**, 11287.

18 T. K. Dargel, R. H. Hertwig and W. Koch, *Mol. Phys.*, 1999, **96**, 583.

19 W. McFarlane, P. D. Akrivos, P. Aslanidis, P. Karagiannidis, C. Hatzisymeon, M. Numan and S. Kokkou, *Inorg. Chim. Acta*, 1998, **281**, 121.

20 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1989, S1–S83.

21 Binding energies were calculated as the difference between the total energy of the fully-optimised complex and the energies of its components optimised using the same basis sets.

22 K. F. Wiley, P. Y. Cheng, M. B. Bishop and M. A. Duncan, *J. Am. Chem. Soc.*, 1991, **113**, 4721.

23 K. F. Wiley, C. S. Yeh, D. L. Robbins and M. A. Duncan, *J. Phys. Chem.*, 1992, **96**, 9106.

24 E. Ortí, P. M. Viruela, J. Sánchez-Marín and F. Tomás, *J. Phys. Chem.*, 1995, **99**, 4955; A. Karpfen, C. H. Choi and M. Kertesz, *J. Phys. Chem. A*, 1997, **101**, 7426.

25 N. DiCesare, M. Belletête, C. Marrano, M. Leclerc and G. Durocher, *J. Phys. Chem. A*, 1998, **102**, 5142; N. DiCesare, M. Belletête, A. Donat-Bouillud, M. Leclerc and G. Durocher, *Macromolecules*, 1998, **31**, 6289.

26 D. Fichou and C. Ziegler, in *Handbook of Oligo- and Polythiophenes*, ed. D. Fichou, Wiley-VCH, Weinheim, 1999, Ch. 4, p. 183.

27 R. S. Rowland and R. Taylor, *J. Phys. Chem.*, 1996, **100**, 7384.

28 The B3P86 functional consists of Becke's three-parameter hybrid functional,[28a] which is a hybrid of Hartree–Fock exchange with local and gradient-corrected exchange and correlation terms, with the nonlocal correlation provided by the "Perdew 86"[28b] expression. (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (*b*) J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.

29 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, GAUSSIAN 98, Revision A.6, Gaussian, Inc., Pittsburgh PA, 1998.

30 P. C. Hariharan and J. A. Pople, *Chem. Phys. Lett.*, 1972, **16**, 217.

31 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270; P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 284; P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.

32 J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, 1954, **22**, 571.

33 H. B. Schlegel, *J. Comput. Chem.*, 1982, **3**, 214.

34 A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899.

35 G. Schaftenaar MOLDEN, CAOS/CAMM Center, The Netherlands, 1991.