On polymerization of some heterocyclic five-membered ring donors in the channels of the three-dimensional coordination polymer [(Me$_3$Pb)$_3$Fe(CN)$_6$]$_\infty$

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Abstract

Various heterocyclic five-membered ring donors have been shown to be completely or partially oxidized within the cavities of the three-dimensional host polymer [(Me$_3$Pb)$_3$Fe^{III}(CN)$_6$]$_\infty$ to give polymeric intercalated or charge transfer complexes respectively. The structure and physical properties of these complexes depend on the type of the heterocyclic species, the time of the reaction, the exposure to light, atmospheric oxygen or moisture and the degree of grinding. Pyrrole, N-methylpyrrole, 2,5-dimethylpyrrole and pyrrolidine polymerize within the cavity of the host polymer to form the corresponding neutral semiconducting diamagnetic polymeric intercalated complexes, the host network being fully reduced to its anionic homologue [(Me$_3$Pb)$_3$Fe^{II}(CN)$_6^-$]$_\infty$. However, if the reaction mixture is treated with a few drops of water, there is a large increase in conductivity, and the complexes become good semiconductors. In contrast, thiazole and thiophene do not polymerize under these conditions, but give paramagnetic charge transfer complexes.

Key words: Lead; Iron; Cyanide; Polymer; Pyrrole

1. Introduction

The electronic and structural characterization of the novel three-dimensional coordination polymers of the type [(R$_3$M)$_3^d$M^{III}(CN)$_6$]$_\infty$ = [^{d}M^{III}(μ-CN–R$_3$M–NC)$_3$]$_\infty$ (^{d}M = Fe, Co or Ru; M = Sn or Pb; R = methyl or butyl) have recently been investigated [1–4]. These complexes are zeolite-like coordination polymers and can oxidize *e.g.* metallocenes, metal iodides and ammonium iodides [5–7]. Furthermore these polymeric complexes behave towards some organic donors [8,9] like *e.g.* iron(III) oxychloride and dichalcogenides containing adjacent layers held together by van der Waals forces [10–12].

The non-superimposable three-dimensional networks of these intercalated polymeric complexes involve Me$_3$M(NC)$_2$ units of trigonal-bipyramidal config-

uration and remarkably wide, almost parallel channels whose walls are internally coated by the Me groups of the lipophilic Me$_3$M units [8]. They are also characterized by the presence of three crystallographically non-equivalent chains $\left[-^d\underset{\wedge}{\overset{\vee}{\text{M}}}-\text{C}\equiv\text{N}-\underset{\wedge}{\text{M}}-\text{N}\equiv\text{C}-\right]_\infty$ in their lattices.

Much work has recently been devoted to the synthesis of new conducting or semiconducting organic polymers [13,14], which have a wide range of applications, such as in microelectronic, display or photovoltaic devices, and chemical sensors [15–17]. One of the most interesting aspects in that area is the electrochemical oxidation of various heterocycles such as pyrrole, thiophene, furan, indole and azulene, which leads to the formation of organic conducting polymers with conductivities ranging from 5×10^{-3} to 10^{+2} Ω^{-1} cm^{-1} [18].

We report here the interaction of some heterocyclic five-membered ring donors as guest materials with [(Me$_3$Pb)$_3$Fe(CN)$_6$]$_\infty$ (**1**) as the three-dimensional host polymer to give a new class of conducting intercalated polymers. To the best of our knowledge, there has

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been no previous report of the oxidative polymerization and conductivity of pyrrole derivatives.

2. Experimental details

The orange precipitate of the host polymer 1 was obtained by mixing aqueous solutions of Me_3PbCl and $K_3Fe(CN)_6$ in 3:1 molar ratio under nitrogen in the dark, washing the product with water and CH_2Cl_2 and drying it under vacuum at room temperature. The purity and identity of 1 were checked by elemental analysis, and IR and UV spectroscopy (Tables 1 and 2). The guest–host intercalated complexes were prepared under strictly anhydrous conditions by adding the dry freshly prepared 1 to an excess of the neat doubly distilled heterocyclic compound, namely pyrrole, N-

methylpyrrole, 2,5-dimethylpyrrole, pyrrolidine, thiophene, thiazole or furan, in the dark under nitrogen with continuous grinding at room temperature. The reaction rate was greatly increased by addition of a few drops of water. The colour and the composition of the intercalated complexes depended on the reaction time. The coloured products of the intercalated complexes were isolated, washed with ethanol and dried in vacuum, and their compositions (2–8) were checked by elemental analysis (Table 1).

The UV spectra were recorded on a Cary 17 spectrophotometer and the IR spectra on a Perkin–Elmer FT-IR-1720 spectrophotometer as KBr discs. The elemental analysis was performed with a Heraeus elemental analyser. The magnetic susceptibility was determined with a Johnson–Matthey susceptometer devised

TABLE 1. Elemental analysis data, composition and other properties of 1 and the intercalated complexes 2-7

Compound	Donor	Composition of the intercalated complexes	Colour	Time and conditions of the reaction	Decomposition temperature (°C)	Analysis: found (calculated) C	H	N
1		$[(Me_3Pb)_3Fe(CN)_6]_\infty$	Orange	In dark	154 [a]–273	18.24 (18.58)	3.02 (2.79)	8.34 (8.67)
2a	Pyrrole	$[(C_4H_3N)_3H^+(1)]_\infty$	Black	At once	Stable up to 350	27.86 (27.70)	3.49 (3.59)	10.74 (10.77)
2b	Pyrrole	$[(C_4H_3N)_3H^+(1)]_\infty 2H_2O$	Black	+H₂O; at once	Stable up to 350	27.11 (27.06)	3.81 (3.28)	10.21 (10.52)
2c	Pyrrole	$[(C_4H_3N)_3H^+(1)]_\infty$	Black	1 day in dark	Stable up to 350	27.78 (27.70)	3.54 (3.59)	10.66 (10.52)
3a	N-methylpyrrole	$[(C_5H_7N)H^+(1)]_\infty$	Black	1 day	301	23.43 (22.86)	3.52 (3.24)	9.06 (9.34)
3b	N-methylpyrrole		Black	4 days in dark		23.40 (22.86)	3.93 (3.24)	9.12 (9.34)
4a [b]	2,5-dimethylpyrrole	$[(C_6H_9N)_{0.5}H^+(1)]_\infty$	Deep red	1 day	280	21.87 (21.27)	3.47 (3.12)	8.82 (8.95)
4b [b]	2,5-dimethylpyrrole	$[(C_6H_9N)H^+(1)]_\infty$	Black–grey	4 days	287	23.92 (23.70)	3.62 (3.41)	9.48 (9.21)
4c [c]	2,5-dimethylpyrrole	$[(C_6H_9N)H^+(1)]_\infty$	Black–grey	10 days in dark	285	23.85 (23.70)	3.92 (3.41)	9.53 (9.21)
4d [c]	2,5-dimethylpyrrole	$[(C_6H_9N)H^+(1)]_\infty$	Black–grey	14 days	285	23.70 (23.70)	4.21 (3.41)	9.63 (9.21)
4e [c]	2,5-dimethylpyrrole	$[(C_6H_9N)_{1.5}H^+(1)]_\infty$	Brown	+H₂O; few hours	290	26.54 (25.93)	3.63 (3.67)	9.77 (9.45)
5	Pyrrolidine	$[(C_6H_9N)_2H^+(1)]_\infty$	Greenish-yellow	1 day	293	25.40 (24.86)	4.08 (4.08)	10.82 (10.08)
6a	Thiophene	$[(C_4H_4S)_{0.1}(1)]_\infty$	Faint yellow	4 days	170 [a]	18.81 (18.92)	3.04 (2.82)	8.57 (8.59)
6b	Thiophene	$[(C_4H_4S)_{0.25}(1)]_\infty$	Yellow	12 days	281	19.38 (19.41)	3.00 (2.85)	8.40 (8.48)
6c	Thiophene	$[(C_4H_4S)_{0.5}(1)]_\infty H_2O$	Greenish-yellow	+H₂O; 12 days	270	19.96 (19.94)	3.06 (2.84)	8.21 (8.16)
7	Thiazole	$[(C_3H_3NS)(1)]_\infty$	Yellow	1 day	212 [a]–305	20.31 (20.50)	2.66 (2.85)	11.04 (9.30)
8	Furan (no reaction)	$[(Me_3Pb)_3Fe(CN)_6]_\infty$	Orange	1 month	154 [a]–273	18.36 (18.58)	3.00 (2.79)	8.39 (8.67)

[a] These compounds undergo colour change under heating.

[b] 4a and 4b: 1 + excess neat doubly distilled 2,5-dimethylpyrrole ⟶ deep red precipitate after 1 day (4a) which turned black after 4 days (4b).

[c] 4c: 1 + 2,5-dimethylpyrrole $\xrightarrow{\text{in dark}}$ red precipitate which turned to deep red and to black after 10 days.
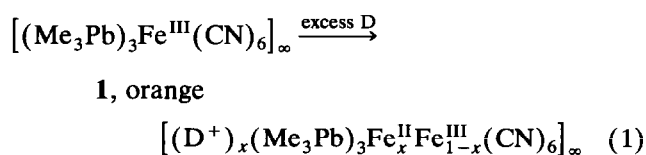
[d] 4d: 1 + oxygen-free 2,5-dimethylpyrrole $\xrightarrow[\text{in dark}]{\text{under N}_2}$ red precipitate which turned to deep red and to black after 14 days.

[e] 4e: 1 + 2,5-dimethylpyrrole $\xrightarrow[\text{in dark}]{\text{H}_2\text{O}}$ brown precipitate after a few hours.

by D.F. Evans. The electrical conductivity at 300 K was measured with a Super Megohmeter model 170, as previously described [8].

3. Results and discussion

The five-membered heterocyclic guest molecules intercalate the host polymer 1 to give intercalated polymeric–charge transfer (CT) complexes:

$$[(Me_3Pb)_3Fe^{III}(CN)_6]_\infty \xrightarrow{\text{excess D}}$$

1, orange

$$[(D^+)_x(Me_3Pb)_3Fe^{II}_xFe^{III}_{1-x}(CN)_6]_\infty \quad (1)$$

2–7, yellow–black $(0 \leqslant x \leqslant 1)$

where x is the number of the donor molecules intercalated within the cavity of the host polymer 1.

The host polymer oxidized the heterocyclic guest donors partially or completely, to give yellow to black intercalated polymeric–CT complexes depending on the degree of CT, the type of the heterocyclic species and the conditions used (Table 1). The CT character of these complexes was supported by the appearance of new absorption bands at around 430 and 720 nm, corresponding to intermolecular CT transitions, and the disappearance (partially or completely) of the band at 420 nm corresponding to $(Fe^{III}(CN)_6)$ transitions

(Table 2). In this case the host polymer 1 is reduced to the isostructural but anionic homologue [(Me₃Pb)₃-Fe^{II}(CN)₆⁻]∞.

The IR spectrum of the host polymer 1 exhibits strong bands at 2120 and 2116 cm⁻¹ due to $\nu(CN)$ and a medium band at 410 cm⁻¹ due to ν_{asym} for the Fe–C bond of the $(Fe^{III}(CN)_6)$ system, in addition to a band at 495 cm⁻¹ due to ν_{asym} of the Pb–C bond. The first two of these bands undergo changes on intercalation with the heterocyclic donor, whereas the $\nu_{asym}(Pb-C)$ band does not show any significant change (Table 2). The IR spectra of the intercalated complexes 2a–2c, 3a, 3b, 4b–4d and 5 reveal intense bands at 2094, 2071, 2058 and 2013 cm⁻¹ and a medium band at 450 cm⁻¹, corresponding to the vibrations of the resulting $(-Fe^{II}(CN)_6)$ system and indicating the absence of Fe^{III} ions (Fig. 1). In these cases, complete CT occurs and $\rho = 1$. On the contrary, the IR spectra of the intercalated complexes 4a, 6 and 7 show bands below and above 2100 cm⁻¹, indicating partial reduction of Fe^{III} ions and consequently partial CT with $\rho < 1$ (Fig. 2). This is also supported by magnetic measurements (Table 2), the intercalated 2a–2c, 3a, 3b, 4b–4d and 5 having diamagnetic properties, and the complexes 4a, 6 and 7 paramagnetic properties [19].

It was previously suggested [19] that pyrrole undergoes spontaneous oligomerization–polymerization when treated with tris-(trimethyltin)hexacyanoferrate.

TABLE 2. Spectral, magnetic and conductivity data for 1 and the intercalated complexes 2–7

Compound	Absorption spectra as KBr disc (nm)	IR spectra (cm⁻¹) [−Fe^{II}(CN)₆]	[−Fe^{III}(CN)₆]	$\nu(C=O)$ (cm⁻¹)	μ_{eff} [μ_B]	σ at $T = 300$ K (Ω^{-1} cm⁻¹)
1	305, 320, 420		2120, 2116, 410		2.57	0.83×10^{-9}
2a		2094, 2058, 2013, 447				0.48×10^{-6}
2b	300, , 700 ᵃ	2071, 2059, 2013, 447		1710	Diamagnetic	0.62×10^{-1}
2c		2092, 2055, 2014, 448				0.62×10^{-6}
3a	300, , 720 ᵃ	2071, 2059, 448		1700	Diamagnetic	0.12×10^{-8}
3b	300, , 720 ᵃ	2074, 2057, 448				0.32×10^{-8}
4a	300, 420, 550	2071, 2059, 2013, 446	2120, 2116		1.86	0.56×10^{-10}
4b	300, 700	2070, 2058, 2012, 450		1700	Diamagnetic	0.51×10^{-8}
4c	305, 700 ᵃ	2070, 2057, 2013, 453		1700	Diamagnetic	0.62×10^{-8}
4d	300, 710 ᵃ	2071, 2058, 2014, 453			Diamagnetic	0.21×10^{-7}
4e	305, 710	2071, 2059, 2012, 448		1700	Diamagnetic	0.32×10^{-5}
5	300, 670 ᵃ	2093, 2072, 2029, 430			Diamagnetic	0.37×10^{-6}
6a	305, 410,	2061	2120, 2116, 410		2.42	0.81×10^{-9}
6b	300, 400, 430	2059, 2026	2120, 2117, 410		2.02	0.97×10^{-9}
6c	300, 400 ᵃ, 440	2070, 2056, 2013, 450	2118, 2115		1.92	0.78×10^{-5}
7	305, 400, 430	2059, 454	2185, 2116		2.02	0.31×10^{-9}

ᵃ Weak intensity.
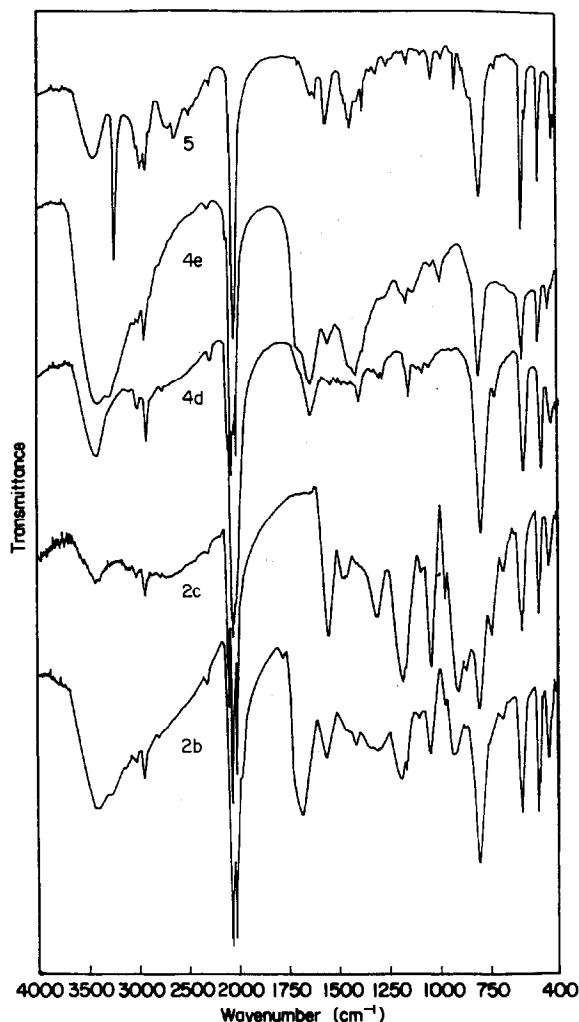
Fig. 1. IR spectra of the polymeric intercalated complexes 2b, 2c, 4d, 4e and 5.
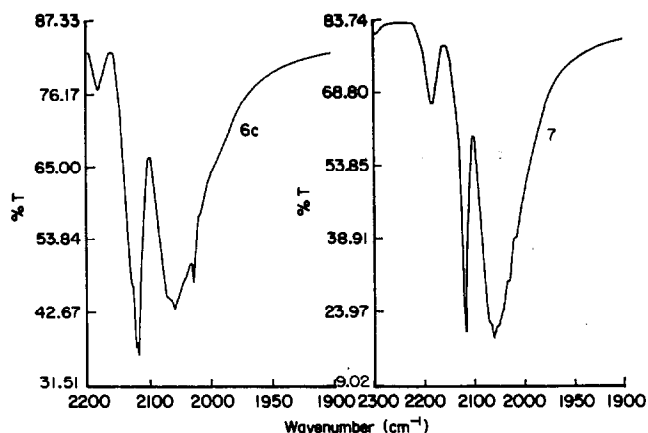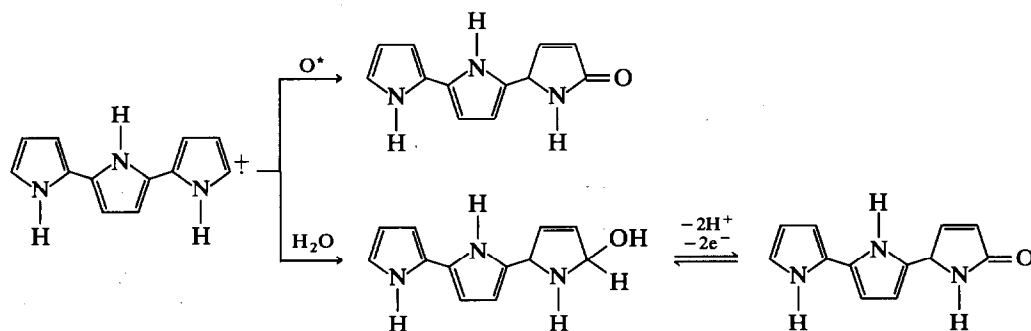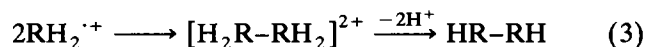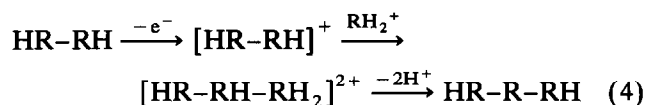

Fig. 2. IR spectra of the CT intercalated complexes 6c and 7.

inorganic solid FeOCl to form a high, electrically conducting polymeric complex; in contrast 2,5-dimethyl-pyrrole does not undergo intercalation into FeOCl [12]. Our observations are consistent with polymerization of pyrrole, *N*-methylpyrrole, 2,5-dimethylpyrrole and pyrrolidine within the cavity of the host polymer 1. Thus pyrroles are chemically oxidized by the host polymer 1 to give free radical cations ($RH_2^{\cdot+}$), which dimerize to form an intermediate dihydro-oligomer dication (i), which then loses two protons to form the neutral oligomer. The neutral oligomer is oxidized more easily than the pyrrole monomers, and takes up a free radical cation ($RH_2^{\cdot+}$) to give an intermediate dihydro-oligomer dication (ii), which is prone to lose two protons to form again neutral, more extended oligomer pyrroles:

The polymerization was assumed to proceed by a free radical mechanism involving formation of repeated di-cation dimers. On the contrary, there has been a report of a structural form of polypyrrole in which intercalation and polymerization of pyrrole had taken place within the constrained van der Waals gap of a layered

$$RH_2 \xrightarrow{-e^-} RH_2^{\cdot+} \tag{2}$$

$$2RH_2^{\cdot+} \longrightarrow [H_2R-RH_2]^{2+} \xrightarrow{-2H^+} HR-RH \tag{3}$$

(i)

$$HR-RH \xrightarrow{-e^-} [HR-RH]^+ \xrightarrow{RH_2^+}$$

$$[HR-RH-RH_2]^{2+} \xrightarrow{-2H^+} HR-R-RH \tag{4}$$

(ii)

The overall polymerization reaction can be represented as follows [13,14]:

$$(x + 2)RH_2 \longrightarrow$$

$$HR-(R)_x-RH + (2x + 2)H^+ + (2x + 2)e^- \quad (5)$$
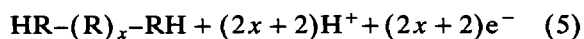
The IR spectra of the intercalated complexes 2–4 exhibit bands at around 1700 cm⁻¹ corresponding to the stretching vibrations of a carbonyl group. This band is absent from the IR spectra of the immediately formed intercalated complex of pyrrole and from that of the complex prepared under nitrogen in strictly dry conditions. This band becomes more intense when a few drops of water are added to the reaction mixture. These observations and the results of the conductivity measurements reveal the occurrence of side reactions when atmospheric oxygen and water molecules are involved in the polymerization process and give rise to carbonyl-substituted polymers. These findings are in agreement with those previously reached on the basis of X-ray photoelectron spectroscopy (XPS) and Fourier transform IR spectroscopy studies [13].

The low conductivity of the intercalated complexes 2–5 reveals that polypyrrole and its derivatives are present in the neutral form within the cavity of the host polymer 1 and that the side reactions reduce to some extent the conductivity of the polymers [13]. In this case, the charge on the host polymer 1 can be compensated by the protons formed in the reaction. The low conductivity is also reflected in the absence of the metallic absorption around 1040 nm in the electronic absorption spectra of these intercalated complexes. Thus these polymeric intercalated complexes behave as weak semiconductors. However, on the addition of a few drops of water to the reaction mixture, a large increase in conductivity occurs, and the polymeric intercalated complexes become good semiconductors (Table 2). Under these conditions the conductivity of 2 increases by six orders of magnitude and those of 4 and 6 by three and four orders of magnitude respectively.

The reaction of 2,5-dimethylpyrrole with 1 involves stepwise formation of the polymeric intercalated complex (Table 1). The IR spectra and the magnetic measurements indicate partial reduction of iron(III) ions in the red CT intercalated complex 4a, and complete reduction to the iron(II) ions in the black polymeric intercalated complexes 4b–4d. The degree of CT is increased by increasing the reaction time or by exposure to moisture, light or atmospheric oxygen, and also by grinding. The addition of water promotes the reaction in which the iron(III) ions are reduced simultaneously to iron(II) ions; the IR carbonyl band appears at 1700 cm⁻¹. The carbonyl band is absent from the IR spectrum of the intercalated complex prepared in the

dark under anhydrous conditions in a nitrogen atmosphere (Fig. 1).

In spite of much evidence that polymerization of pyrroles involves reactions at the α- and α'-carbon atoms, 2,5-dimethylpyrrole is polymerized within the cavity of the host polymer 1. The hypothesis of α–α' polymerization of pyrroles has been supported by oxidative degradation studies of chemically prepared polypyrroles or pyrrole blacks, which lead predominantly to pyrrole-2,5-dicarboxylic acid [20], and by the fact that 2-substituted pyrroles do not undergo electropolymerization [21]. Nuclear magnetic resonance (NMR) studies [22] also point to α,α'-linked polypyrroles. However, more recent XPS studies [23] have shown that as many as one in three pyrrole rings is affected by structural disorder, part of which may be attributed to non-α,α' linkages, the non-regular linkage leading to poor crystallinity of polypyrrole. Also, INDO calculations predict that monomer radical cations could in principle undergo radical coupling reactions at either the α or the β positions of these oligomeric radical cations [14]. Furthermore, oxidation of 2,5-diphenylpyrrole gives a mixture of products involving a dimeric product linked via the β position [24]. In view of these facts, and the observation that the polymeric intercalated complexes 4b–4e are black and show the same features in the IR and UV spectra as the polymeric intercalated complexes 2 and 3, as well as the same diamagnetic and conductivity characteristics, it can be concluded that polymerization of 2,5-dimethylpyrrole occurs within the cavities of the host polymer 1.

In the case of pyrrolidine, there have been no previous reports of its chemical or electrochemical polymerization. It is assumed that it must be partially oxidized by the iron(III) ions of the host polymer 1. However, complete CT occurs, to give a greenish-yellow precipitate, which adheres strongly to the glass surface, is diamagnetic and has a conductivity more or less equal to that of 2. These results, as well as elemental analysis, support the view that polymerization of pyrrolidine occurs within the cavities of the host polymer 1. The polymeric intercalated complex 5 seems to be more stable towards atmospheric oxygen than do complexes 2–4. The band due to ν(C=O) does not appear in the IR spectrum of 5, and the greenish-yellow colour resembles that of films of neutral polypyrrole prepared in a dry-box, which turn black after exposure to oxygen for a few minutes.

In contrast, thiazole and thiophene do not undergo polymerization within the cavities of 1 under the experimental conditions used owing to their high oxidation potentials which are 1.45 and 1.60 V (with respect to a saturated calomel electrode (SCE)) respectively, com-

pared with the 0.8 V(SCE) for pyrrole. They form CT intercalated complexes. Furan fails to interact with **1** because it has a higher oxidation potential of 1.85 V(SCE) [18].

Acknowledgments

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