INTERCALATION OF POLYFURAN IN FeOCl.

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ABSTRACT

The intercalation of polyfuran, by in-situ intercalative oxidative polymerization of terfuran in FeOCl is reported. The intercalation reaction proceeds to completion in methanol in a sealed tube at 100 °C. The resulting compound, polyfuran/FeOCl (I), is crystalline. An interlayer expansion of ~7.7 Å is observed upon intercalation. The formation of polyfuran in the interlayer space of the host material was confirmed by FTIR spectroscopy and by isolation of the polymers from the host. Tetrafuran could not be intercalated completely under the conditions employed. Electrical conductivity and thermoelectric power data from pressed pellets of (I) are reported and the results are compared with other FeOCl intercalated polymers. X-ray diffraction, magnetic, infrared spectroscopic and scanning and transmission electron microscopic characterization of (I) are reported.

1. Introduction

FeOCl is one of the most convenient redox-intercalation hosts for a great variety of organic molecules including conducting polymers. The in-situ intercalative polymerization of pyrrole, 2,2'-bithiophene and aniline in the interlayer space of this material has been reported. The resulting intercalation compounds are indeed intriguing systems of theoretical and practical interest, composed of alternating monolayers of positively charged conductive polymer and negatively charged FeOCl. Intercalated polymers in structurally defined hosts may be amenable to structural characterization by crystallographic methods. They also represent a new class of materials with anisotropic properties derived from the different structural and electronic nature of their individual components. It should be noted that the mechanism of this intercalative process is not well understood. As part of our general investigations in this
area we examined the redox-intercalative behavior of furan oligomers with FeOCl. We found that the intercalated organic species is polyfuran (Pfu), a known (but not extensively studied) conductive polymer. We report here chemical, physical and electrical characterization of the Pfu/FeOCl intercalates.

2. Experimental Section

2.1 Reagents The reagents FeCl₃ and Fe₂O₃ were purchased from commercial sources and were used without further purification. FeOCl is prepared by heating at 380 °C in a sealed pyrex tube a mixture of FeCl₃ (anhydrous) and Fe₂O₃ in 1.2:1 ratio. The purple FeOCl crystals are isolated by washing away the excess FeCl₃ with acetone and ether.

Synthesis of 2,2':5',2"-Terfuran To a cooled solution of 1,4-bis(2-furyl)-1,4-butanedione (10 g, 45.9 mmol) in acetic anhydride (300 mL) was added concentrated hydrochloric acid (15 mL) portion-wise. The solution was poured into water (600 mL) and stirred for 1 h. The aqueous solution was extracted with CCl₄ (4x150 mL). The combined organic layers were washed successively with water, saturated NaHCO₃ solution and saturated NaCl solution. After drying over anhydrous MgSO₄, the solvent was removed in vacuo to give a brown oil which was purified by flash column chromatography over silica gel using Et₂O:hexanes (v/v=1/5) as eluent to give 5.8 g (63%) of α-terfuran as white solid: m.p. 63-64°C; H NMR: δ 6.45 (dd, J=3.3, 1.8 Hz, 2H), 6.58 (s, 2H), 6.60 (d, J=1.7 Hz, 2H); C NMR: δ 105.40, 106.91, 111.43, 141.93, 145.72, 146.25; MS: m/e (rel. intensity) 200 (M⁺, 100), 115 (22); UV-vis: λmax (εM) 330 (1.66x10⁴), 350 (1x10⁴).

2.2 Reaction of terfuran with FeOCl 0.3 g (2.8 mmole) of FeOCl and 0.2 g (1 mmole) of terfuran were mixed with 1.5 mL MeOH, frozen in the bottom of a pyrex tube which was subsequently flame-sealed under reduced pressure. The tube was heated at 100 °C for 6 days. The black shiny solid was isolated by filtration washed with acetone and dried in vacuum. Elemental analytical data show that the formula is (C₄H₂O)ₓFeOCl (I) with x ranging between 0.67-0.75.

2.3 Synthesis of doped polyfuran This reaction was run under nitrogen atmosphere. 0.3 g (1.5 mmole) of terfuran was dissolved in 50 mL CH₃CN, and to that was added 1.5 g (9.5 mmole) of FeCl₃. The mixture was stirred at room temperature for 9 hours. The black solid was isolated by filtration in air. It was washed with H₂O and acetone, and dried in vacuum.

2.4 Physical Measurements X-ray diffraction experiments were carried out with a Phillips XRG-3000 instrument using CuKα radiation. Fourier transform infrared spectroscopy (FTIR) was performed with a Nicolet 740 FTIR spectrometer. Magnetic susceptibility measurements were done with a S.H.E. Corp. SQUID susceptometer in constant magnetic field. Direct current electrical conductivity and thermopower measurements were obtained from 5 to 320 K using a data acquisition and analysis system described elsewhere. Samples were measured as pressed pellets using conditions and
protocols described earlier.\textsuperscript{7b} Scanning electron microscopic (SEM) and transmission electron microscopic (TEM) studies were performed on JEOL-JSM35CF and JEOL-100CX-(II) instruments respectively.

3. Results and Discussion

3.1 Synthesis and Characterization

In this study we used furan, terfuran and tetrafuran as molecules for intercalation in iron oxychloride. These species are known to oxidatively polymerize chemically or electrochemically to yield polyfuran\textsuperscript{5}, according to eq. 1.

\[
\begin{align*}
2e^- \text{oxidation} & \rightarrow \overset{\circ}{\text{Furan}}_n \\
\text{Eq. 1}
\end{align*}
\]

Not surprisingly, furan itself did not intercalate in FeOCl because of its high oxidation potential.\textsuperscript{5} The redox potentials of terfuran and tetrafuran are \(-1.3\) and \(-1.0\) volts vs. SCE respectively. These values are low enough to be suitable for redox intercalation chemistry with FeOCl. Terfuran reacts slower with FeOCl than pyrrole or 2,2'-bithiophene, presumably because of its larger size. In the beginning stages of this work we used acetonitrile as solvent and reflux in air but we failed to obtain a completely intercalated product reproducibly, even after several weeks. Perhaps the limited amount of available terfuran did not allow its use in great stoichiometric excess as it is usually necessary with 2,2'-bithiophene and aniline.\textsuperscript{2, 3} As a result, we tried methanothermal conditions (sealed tube, 100 °C) in order to force the reaction to completion. In the intercalated product the FeOCl layers are expanded by \(\sim 7.7 \AA\) to accommodate the intercalated polyfuran species. Sonication of the FeOCl in methanol for \(\sim 2-3\) min was found to accelerate the reaction considerably. The intercalation was deemed complete when the 002 reflection of FeOCl disappeared completely from the X-ray powder diffraction pattern of the product. The X-ray powder diffraction patterns are usually broad, indicating significant disruption of the stacking of the FeOCl layers, see figure 1.

\[
\begin{align*}
\text{Figure 1. Typical X-ray powder diffraction pattern of (I)}
\end{align*}
\]
Tetrafuran intercalated partially when it was heated with FeOCl in methanol in a sealed tube at 100 °C. It did not intercalate when refluxed in acetonitrile. Tetrafuran could not be intercalated completely under the conditions employed. This was attributed to the large size of this monomer and the resulting exceedingly slow kinetics of the reaction.

The crystalline nature of (I) is also evident in the SEM images of the samples which also show the absence of impurity amorphous phases, see Figure 2 for a typical sample. Selected area diffraction (SAD) patterns of (I) obtained from TEM studies show clearly the structural integrity of the material is maintained after intercalation. Figure 3 shows a SAD pattern of the (h0l) zone with diffraction spots which can be indexed according to the original a- and c- axes of the FeOCl lattice. This is consistent with the expected invariance of the a- and c- axes of the crystal upon intercalation. The ordering of the polyfuran chains in the intralamellar space remains unknown as no diffraction spots corresponding to a superlattice are evident.

![Figure 2. SEM photographs of FeOCl crystals intercalated with polyfuran.](image)

### TABLE I Comparison of the FTIR-spectra of (Pfu)/FeOCl (I), Bulk polyfuran and polyfuran extracted from (I). Energies are given in cm⁻¹.

<table>
<thead>
<tr>
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<th>(Pfu)/FeOCl</th>
<th>Bulk polyfuran</th>
<th>Extr. Polyfuran</th>
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<tbody>
<tr>
<td>m 1527</td>
<td>m 1527</td>
<td>m 1534</td>
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<tr>
<td>m 1492</td>
<td>m 1499</td>
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<td>s 1436</td>
<td>s 1450</td>
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<td>s 1238</td>
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<td>s 1175</td>
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<td>s 1048</td>
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<td>s 999</td>
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<td>m 929</td>
<td>s 936</td>
<td>s 922</td>
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<td>m 879</td>
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<td>w 823</td>
<td>vs 774</td>
<td>vs 774</td>
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<tr>
<td>w 731</td>
<td>vs 464</td>
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vw=very weak, w=weak, m=medium, s=strong, vs=very strong
The Fourier transform infrared spectrum (FTIR) of (I) is shown in figure 4, and it shows absorptions both from the organic and FeOCI portions of the material. The presence of polyfuran in (I) is apparent when comparing its FTIR spectrum with that of chemically prepared bulk polyfuran and that of polyfuran extracted from (I). The energies of IR absorptions are given for comparison in Table I. The molecular weight of polyfuran in (I) and its average chain length are not known at this stage. However, they are expected to be small due to the large relative size of terfuran monomer and the constrained intralamellar environment in which it must oxidatively couple. These two factors would slow the coupling kinetics considerably and would inhibit extensive polymerization.

Figure 3. Selected area diffraction pattern of (I) with the beam perpendicular to the (101) plane.

Figure 4. FTIR spectrum (KBr pellet) of (I).

Variable temperature magnetic susceptibility data for (I) are shown in figure 5. The magnetic properties of the reduced FeOCI layers dominate in (I). The effective spin-only magnetic moment at room temperature is 3.0 BM and it decreases with falling temperature. This value is well below 5.9 BM (had the material been paramagnetic) and it is in good agreement with other intercalates of FeOCI. The steady decrease of \( \mu_{\text{eff}} \) with temperature indicates strong antiferromagnetic exchange. It should be noted that the magnetic properties of FeOCI itself and its intercalates are not well understood at present. Detailed magnetic and Mössbauer studies will be published elsewhere.
3.2 Charge Transport Properties

Electrical conductivity data on pressed pellets of (I) show a room temperature value in the range of $10^{-3}$ to $10^{-4} \Omega^{-1} \text{cm}^{-1}$ and thermally activated behavior. The general behavior is thermally activated charge transport, similar to that observed in other intercalated conductive polymers. However, (I) is considerably less conductive when compared to its polypyrrole and polythiophene analogs. A possible reason for this may be the anticipated shorter chain-lengths of polyfuran in (I).

The thermoelectric power of (I) is positive at room temperature (~7 $\mu$V/K) and increases linearly with falling temperature reaching the value of 45 $\mu$V/K at 230 K (see figure 6). This behavior suggests a p-type semiconductor and it is distinctly different from the p-type metallic character found previously in polypyrrole/FeOCl and polythiophene/FeOCl. Similar temperature dependence of the thermopower was found in the p-type semiconductor (ferrocenium)$_{0.50}$FeOCl. In the latter, the charge transport occurs exclusively through the FeOCl layers. Based on the thermopower results, it is likely that in (I) the FeOCl section, rather than polyfuran, is responsible for the charge transport properties. The reason for this, may be the short chain length of the intercalated polyfuran which would inhibit facile chain to chain charge transport. Short chain lengths are expected considering that terfuran is a relatively large molecule and its
reactivity will slow down significantly in the constrained intralamellar space of the host thus avoiding extensive polymerization.

Acknowledgement. Financial support from the National Science Foundation (grant DMR-8917805 to MGK) is gratefully acknowledged. At Northwestern University support was provided by ONR; this work made use of Central Facilities supported by NSF through the Materials Research Center.

REFERENCES


