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Electronic and Ionic Transport in Processable Conducting Polymers

by

Martin Pomerantz, Grant Administrator

John R. Reynolds

Krishnan Rajeshwar

Dennis S. Marynick

Center for Advanced Polymer Research

Department of Chemistry

Box 19065

The University of Texas at Arlington

Arlington, TX 76019-0065

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Fei Wang and John R. Reynolds

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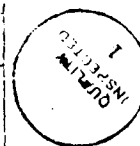
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Polymers Prepared Via Metal Complexation Polymerization

Fei Wang and John R. Reynolds*

*Center for Advanced Polymer Research, Department of Chemistry
The University of Texas at Arlington
Arlington, Texas 76019-0065*

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INTRODUCTION

A variety of metal complex polymers, incorporating square-planar MS_4 metal centers into conjugated ligands, have been prepared with the goal of preparing materials with elevated electrical conductivity, along with novel magnetic and optical properties. These include poly(metal tetrathiooxalates),¹⁻³ poly(metal ethylenetetra-thiolates),⁴⁻⁶ poly(metal tetrathiosquarates),⁷ poly(metal tetrathiafulvalenetetra-thiolates),^{8,9} poly(metal tetrathianaphthalenes),¹⁰ and poly(metal benzenetetra-thiolates).¹¹ These materials tend to be insoluble and infusible powders which precipitate during complexation polymerization of transition metal ions with highly reactive thiolate ligands. In addition, they have a very low crystallinity, tend to be paramagnetic, and are strong absorbers of infrared radiation making structural characterization by x-ray diffraction, NMR spectroscopy and IR spectroscopy difficult, if not impossible. During synthesis some of these systems possess solubility, which can be attributed to the high charge density along the polymer backbone, but precipitation to amorphous powders prohibits resolubilization. When these planar conjugated ligands are complexed in a square planar coordination with transition metal ions [e.g. Ni(II), Pd (II) or Pt (II)] the molecular structure is quite rigid and "ribbon-like". In fact, for the specific case of poly(metal tetrathiooxalates), which can have conductivities as high as $10^{+2} \Omega^{-1} \text{cm}^{-1}$, we find low degrees of polymerization and stacked/sheet like model structures.³

In order to circumvent the low solubility of these fully conjugated polymers, we have been incorporating square planar metal complexes, specifically metal bis(dithiolenes), into the main chain of polymers that contain flexible units. Our initial work in this field was recently communicated by reporting the synthesis of poly([1,1'-oxybis[4-(1,2-dithiolatoethenyl)-benzene]]nickel (II)) (PBOSD-Ni).¹² This polymer, as illustrated in Structure 1 where $R=O$ and

insert structure 1

$M=Ni$, is highly soluble in a variety of solvents in the as prepared, reduced, form with two negative charges associated with each nickel bis(dithiolene) unit. In this form the polymer can be redissolved repeatedly. The oxidized and neutral form of the polymer, with a zero net charge on

each metal bis(dithiolene), is only sparingly soluble (10^{-5} M) in DMF and completely insoluble in most other solvents.

Here we report on the synthesis and characterization of a series of polymers having the general form of Structure 1 via transition metal complexation polymerization. In this instance we vary the flexible linkage (R) to include -O-, -S-, -CH₂-, -(CH₂)₁₀-, -(CH₂)₂₂- and -(OCH₂CH₂)₃O-. Both the nature of the flexible linkage and the oxidation state of the metal complex are found to impact both the solubility and optoelectronic properties of the polymers.

RESULTS AND DISCUSSION

Ligand Syntheses. The synthesis of a series of bis(aryl dithiocarbonates) was carried out as outlined in Scheme I with *p*-phenyldithiocarbonate moieties separated by a variety of flexible

insert scheme I

linkages. The -O-, -S- and -CH₂- linkages were introduced by beginning with diphenyl ether (2a) diphenyl sulfide (2b) and diphenyl methane (2d) respectively. The -(CH₂)₁₀-, -(CH₂)₂₂- and oligomeric ether chain -(OCH₂CH₂)₃O- linkages were introduced by preparation of 2c, 2e and 2f as outlined in Scheme II. Compound 2c was prepared using a conventional Williamson

insert scheme II

etherification from phenol and 1,2-bis(2-chloroethoxy)ethane. Compound 2e was prepared via a Friedel-Crafts acylation of benzene with sebacoyl chloride, followed by a Wolff-Kishner reduction. The synthesis of 2f was also carried out in two steps. The first reaction was effected by initially reacting benzyl magnesium chloride with 1,10-dibromodecane in the presence of a catalytic amount of lithium tetrachlorocuprate,¹³ which proved to be a convenient route to preparing mono bromo-terminated alkanes. Wurtz coupling of 7 give the required product 2f separating two phenylenes with 22 methylene carbons.

The bis(dithiocarbonates) were then prepared using a modification of methods developed for the synthesis of substituted styryldithiocarbonates.^{14,15} Starting with 2, Friedel-Crafts acylation with chloroacetyl chloride in the presence of AlCl₃ led to 3. Bromoacetyl bromide and

bromoacetyl chloride were also used as acylating reagents, but significantly lower yields of product were obtained. In the case of **2c** as starting material, the polyglycol ether chain could potentially complex with the AlCl_3 , and we found that an extra amount of AlCl_3 and more vigorous conditions of refluxing were required to force the reaction to completion. Compound **3** was subsequently reacted with the potassium salt of *O*-ethyl xanthic acid in acetone to give **4**. The potassium chloride that precipitated from the reaction mixture facilitated driving the reaction to high yield. The final step involves a cyclization reaction of the xanthate ester, **4**, with HBr in acetic acid to give the desired dithiocarbonates **5**. Both 30% HBr in acetic acid and 48% HBr in water were used, with the acetic acid HBr solution giving better results. In the case of **5c**, the polyether tended to cleave with HBr. Milder reaction conditions were employed in this case but lower yields of product were obtained.

The structures of all bis(dithiocarbonates) **5a-f** were confirmed by IR, ^1H NMR, ^{13}C NMR and elemental analysis. All of the IR spectra of **5** exhibit a band at about 1635 cm^{-1} for the $\text{C}=\text{O}$ stretch confirming formation of the dithiocarbonate. Common features in the ^1H NMR spectra are one singlet at $\delta=6.8$ ppm corresponding to the olefinic proton and an AA'XX' and AA'BB' system in the aromatic range corresponding to the 1,4-substituted benzene ring. Compound **5b** exhibits only one singlet for all the aromatic protons. Common features in the ^{13}C NMR spectra are a peak at 192 ppm assigned to the carbonyl and six peaks in the aromatic and olefinic range.

Tetrathiolate formation. The preparation of polymeric metal bis(dithiolenes) via transition metal complexation polymerization first requires the formation of a highly reactive tetra-anionic

insert scheme III

ligand as shown in Scheme III. As described previously,¹² we have determined the experimental conditions necessary for complete cleavage of the bis(dithiocarbonates) to the tetrathiolates by synthesizing the tetramethylated species (**8**). In fact, we have obtained **8** in quantitative yields as described in the Experimental Section. This is important in that incomplete conversion may limit molecular weight or possibly lead to monodentate as opposed to bidentate chelating ligands. Up to

four monodentate ligands could potentially react with each transition metal ion leading to a highly crosslinked, and completely insoluble structure.

These problems were observed for the case of tetrathiapentalenedione (9), which serves as a precursor to ethylenetetrathiolate (10) as outlined in Scheme IV. One study⁶ described the "half-

insert scheme IV

opening" versus "full-opening" of the tetrathiapentalenedione. Gel formation has also been observed in the synthesis of metal complex polymers of ethoxide treated 9 with elemental analysis indicating that stoichiometric formation of 10 did not occur.¹⁶

All results point to the fact that the tetraanionic ligands are extremely sensitive to oxidation. Even when small amounts of oxygen are present during ethoxide cleavage reactions insoluble polymeric product forms, most likely through the formation of bisulfides. For this reason, all thiolate ligand formation and metal complex polymerizations were carried out in degassed ethanol and using scrupulously deoxygenated nitrogen.

Metal Complexation Polymerizations. Polymerization reactions were carried out at 60°C by conversion of 5 to tetrathiolate, followed by reaction with a stoichiometric amount of NiBr₂ overnight as shown in Scheme V. In the cases of 5a, 5b and 5d, in which short spacers

insert Scheme V

(-O-, -S- or -CH₂-) were present in the ligands, a homogeneous dark brown solution of polymer was obtained. On the other hand when 5c, 5e and 5f was used, a small amount of dark brown solid precipitated out of solution and thus the longer spacers reduced the solubility of these polymers in ethanol. All of the reaction solutions were found to exhibit a typical nickel bis(dithiolene) complex UV-Vis-NIR spectra [λ_{max} (ethanol) 215, 270, 310, 490, 930 nm]¹⁷⁻¹⁹ which indicates that the polymers formed contain the desired nickel bis(dithiolene) units. We term these the reduced form of the polymers since each nickel bis(dithiolene) site is dianionic and can be represented as [NiL₂²⁻]_n. For the polymer from 5a, the reduced form of the polymer is also soluble in water, acetonitrile, acetone, and DMF.

The reduced form of all polymers have proven to be air unstable and were oxidized by either air or iodine to yield black solid powders (oxidized form) which are insoluble in most solvents. The oxidized form of all of the polymers do slightly dissolve in DMF to form brown solutions, but **11d-f** (containing non-polar linkages) have a lower solubility in DMF than **11a-c** (containing polar linkages) and cannot completely dissolve. Polymer **11c**, containing the polyglycol chain, exhibits a better solubility in DMF than all of the other polymers investigated and is also slightly soluble in THF. The alkane linkages in the polymer chains of **11e** and **11f** reduce their solubilities in DMF but increase their solubilities in toluene, xylene, and THF. When dissolved in these solvents, green colored solutions are obtained. Thus, as expected, the nature of the flexible linkage plays an important role in controlling the solubility of these polymers with non-polar linkages improving solubility in non-polar solvents and polar linkages improving solubility in polar solvents. Polymers **11e** and **11f** were fractionated by extraction with hot THF, showing about 20% of polymer to be soluble while the other 80% remained insoluble. A GPC analysis on these THF solutions shows a series of separated peaks corresponding to different chain length oligomers. Comparison of these GPC retention times for that found for monomeric model compounds prepared in our laboratory suggest the soluble fraction to contain up to about hexamers. We expect the 80% remaining insoluble fraction to have a higher degree of polymerization. Elemental analyses of all polymers (**11a-f**) were found to differ somewhat from that calculated for a neutral polymeric repeat unit (see Experimental Section). This is not surprising considering end-group contributions in these oligomers and the possibility of incomplete oxidation of each metal center.

One explanation for the low solubilities of these polymers in the oxidized state is the strong potential for metal-metal and metal-sulfur interactions between molecules. In order to reduce the regularity of the spacer in the ligand along the polymer chain, mixed ligand polymers were prepared using equal amount of **5c** and **5f** in the polymerization process. Unfortunately, the resulting polymers had no significant improvement in solubility.

All of the polymers in the oxidized form have two intense IR bands at $1367 \pm 3 \text{ cm}^{-1}$ and $1190 \pm 2 \text{ cm}^{-1}$. These absorbances are attributed to the nickel bis(dithiolene) complex and are combination bands. A qualitative assignment for the 1367 cm^{-1} peak is a vibration predominantly from the perturbed C=C stretch, and the 1190 cm^{-1} peak is that of the perturbed C=S stretch.²¹ These IR results further confirm the formation of nickel bis(dithiolene) units in the polymer chain and retention of the nickel complex in the oxidized (neutral) form.

Optical Properties. All of the polymer solutions show a near IR absorbance peak maximum at ca. 900 nm which is assigned to the $2b_{1u} \leftrightarrow 3b_{2g}$ transition^{21,22} This is shown in Figure 1 for polymer 11c where the near-IR absorption is separated from the higher energy absorptions by a relatively broad window from 600-750 nm. Numerous applications exist for materials which can selectively filter/absorb near-IR while being relatively transparent in the visible region.²³ These include filters of IR sensitive materials, heat cut-off, materials and as materials addressable by semiconductor (e.g. GaAs based) laser diodes.²⁴ The ability to directly cast films of polymers containing these near-IR absorbers may ultimately lead to films significantly more homogeneous than dye impregnated thermoplastics.²³

The position of the near-IR peaks are affected by solvent polarity. For example, Table I

insert Table I

shows the near-IR results for the polymer having the nickel bis(dithiolene) complex separated by 10 methylene units. Increasing solvent polarity shifts this absorption significantly further into the near-IR with a maximum shift of 94 nm observed when the solvent is changed from toluene to dimethyl sulfoxide. Simultaneously, a color change is observed as the toluene solutions are green and the HMPA, DMF and DMSO solutions are brown. Normally, the color of the complex solution indicates the oxidation state of the nickel bis(dithiolene) complex. Neutral forms are usually green in color while anionic forms are red-brown. Previous studies have shown that the neutral form of the nickel complex can be reacted with a number of nitrogen bases (e.g., pyridine, or hydrazine) forming salts of the nickel complex ions.²⁰ A study on a monomeric model compound shows that the oxidized form dissolved in DMF was green in color initially, but

changed to brown in less than a hour. At the same time a shift of the NIR peak from 855 nm to 905 nm was also observed. In the case of DMF, the presence of traces of dimethyl amine (a degradation product) may account for a partial reduction of the complex and the observed spectroscopic shift. The fact that significant spectral changes are observed in the highly polar, yet non-reducing, solvents HMPA and DMSO verifies that the solvatochromic behavior is due to solvent polarity.

Electrochemical Properties. These polymeric nickel bis(dithiolene) complexes all exhibit two separate redox processes as shown in Scheme VI. As prepared, each metal complex is dianionic and stable in nonoxidizing solvents. A cyclic voltammogram of polymer **11c** is shown in Figure 2 to exemplify the electrochemical behavior of these polymers. At potentials equal to and cathodic of -1.0 V the polymer complex remains in the dianionic state. Scanning anodically the polymer exhibits two redox processes at $E_{1/2} = -0.71$ V and at $E_{1/2} = +0.19$ V. These two processes are reversible as evident by the 60 mV and 75 mV peak to peak separation seen for each process respectively. Referring to Scheme VI, these redox processes can be assigned to the reversible oxidation of the dianion to the monoanion and finally to the neutral state. During both of these processes the polymer remains in solution. This is shown in Figure 3 as the scan rate (ν) dependence of the peak current (i_p). Diffusion controlled processes typically exhibit an i_p that is linearly dependent on $\nu^{1/2}$ while surface confined species exhibit i_p dependent on ν . The observed linear dependence of i_p on $\nu^{1/2}$ for both processes and both anodic and cathodic current between 40 mV S^{-1} and 200 mV S^{-1} shows that the polymer does not deposit on the electrode surface at potentials cathodic of +0.5 V. The pattern of this redox behavior is consistent with non-polymeric nickel bis(dithiolene) complexes investigated previously²⁵ illustrating that, though the metal complexes are contained in the polymer backbone in our case, the metal centers approach the electrode surface close enough for electron transfer.

In the case of polymer **11a** further anodic scanning beyond +0.2 V significantly distorts the symmetry of the $[\text{NiL}_2^{1-}] \rightleftharpoons [\text{NiL}_2^0]$ process by increasing the current during reduction of the

neutral form.¹² This was especially evident for the polymer containing only an oxygen flexible linkage as it is precipitating onto the electrode surface in the neutral form.

Electrical Properties. Attempts were made to prepare free standing films by casting from DMF solutions. The materials were quite brittle, cracking easily. Electrical conductivities were subsequently measured on pressed pellets. As expected for a polymer metal complex system with a low extent of conjugation, the conductivities are quite low. For example, polymer 11a exhibits a room temperature conductivity of $10^{-6} \Omega^{-1} \text{ cm}^{-1}$. It has been found that most metal bisdithiolenes have conductivities lower than $10^{-5} \Omega^{-1} \text{ cm}^{-1}$ independent of the identity of the central metal atom and oxidation state.²⁶ Recently Underhill et al have reported on certain maleonitrile salts that can be metallic.²⁷⁻²⁹ The ability of these complexes to stack, form direct metal-metal bonds and attain the proper partial oxidation state are all required for high conductivity.

Disorder present in the polymers discussed here prevents significant inter-chain stacking. In fact, an x-ray powder spectrum of polymer 11a showed only an amorphous halo centered at about 19 degrees. In addition, the flexible spacers inhibit any conjugation along a single chain and facile charge transport is prohibited. Thus, the low observed conductivities are as expected.

Conclusions

A series of polymers, containing nickel bis(dithiolene) complexes in the main chain, have been prepared via metal complexation polymerizations with flexible linkages between the complexes ranging from one atom (-O-, -S-) up to 22 atoms [-(CH₂)₂₂-]. The polymers are highly soluble in a number of solvents in the as-made reduced (dianionic) form. While oxidation of the metal centers to the essentially neutral form is found to decrease the overall solubility, polymers containing long flexible linkages are more soluble than those containing short linkages. The electrochemical and spectral properties of the polymers are consistent with a stable main-chain nickel bis(dithiolene) structure where the metal complex can attain -2, -1 and neutral oxidation states. Due to the nature of these metal complexation reactions, especially problems encountered in

obtaining stoichiometric balance of functional groups during polymerization, the materials are most likely oligomeric.

Experimental Section

General. All water and air sensitive liquids were transferred either with cannulae or with syringes. Air and moisture sensitive reactions were carried out with the use of standard inert atmosphere techniques. All melting points are uncorrected. Infrared spectra were recorded on a Digilab FTS-40 FT-IR spectrophotometer. Low-field (60 MHz) proton NMR spectra were run on a Varian EM 360 spectrometer. High-field (200 MHz and 300 MHz) ^1H and ^{13}C NMR spectra were recorded on a Nicolet NT-200 spectrometer or an IBM-Bruker spectrometer in chloroform- d solutions. Chemical shifts are reported referenced to tetramethylsilane or chloroform- d (77.0 ppm for ^{13}C). HPLC was performed with a Waters 440 HPLC system. UV-Vis-NIR spectra were run on a Varian 2300 spectrophotometer. Powder X-ray diffraction was carried out on a Phillips APD-3600 diffractometer using Cu K α radiation and a 2θ scanning mode. GPC was performed on a Waters 840 GPC systems. Electrochemical measurements were obtained using an EG&G Princeton Applied Research Model 273 Potentiostat/Galvanostat. Elemental analyses for carbon and hydrogen were carried out on a Perkin-Elmer 2400 CHN Analyzer.

Materials. Ethanol was distilled from magnesium and degassed by three freeze-pump-thaw cycles. THF was distilled from potassium benzophenone. All other solvents were distilled from calcium hydride prior to use. Nitrogen was purified using an Alfa De-Ox deoxygenation catalyst train.

All analogous compounds were prepared in a similar manner so only the **a** series are described in detail. For those compounds prepared using a different procedure details are included.

Triethylene glycol diphenyl ether (2c). A mixture of phenol (66.9 g, 0.711 mol), KOH (43.9 g, 0.782 mol) and butanol (300 ml) was stirred and heated to reflux. A solution of 1,2-bis(2-chloroethoxy)ethane (69.2 g, 0.370 mol) in butanol (30 ml) was added dropwise to the

mixture over a period of 2h. The resulting mixture was heated to reflux for 10 h. Concentrated HCl was added to acidify the mixture. After reaction, distillation was used to remove some of the butanol (ca. 120 ml), and water (200 ml) was added to the mixture. The resulting mixture was extracted with ether (3 x 150 ml), the ether solutions combined, washed with water (3 x 100 ml), dried (magnesium sulfate), concentrated, recrystallized (hexane), and dried to give 68.3 g (63.6%) of **2c**: mp 37-40 °C; ¹H NMR (60 MHz) δ 3.72 (s, 4 H), 3.8-4.0 (m, 4 H), 4.0-4.2 (m, 4H), 6.8-7.4 (m, 10 H).

1,10-Diphenyl-1,10-decanedione (6). Compound **6** was prepared³⁰ by reacting, sebacoyl chloride (47.8 g, 0.20 mol, 92% pure) with excess benzene (265 g, 3.4 mol) as both reagent and solvent and AlCl₃ (60 g, 0.45 mol) as catalyst. 45.2 g (76.1%) of **6** was isolated. ¹H NMR (60 MHz) δ 1.4-1.8 (m, 12 H), 2.86 (t, 4 H, J=6.5 Hz), 7.0-7.4 (m, 6 H), 7.6-7.9 (m, 4 H).

1,10-Diphenyldecane (2e). The standard Huang-Minlon modification of the Wolff-Kishner reduction was followed. KOH (50 g, 0.77 mol) was dissolved by warming in diethylene glycol (300 ml) in a 500 ml flask. Compound **6** (45 g, 0.139 mol) and 85% hydrazine hydrate (40 ml) were added to this at 100 °C and refluxed for 1 h. 60 ml of an H₂O/diethylene glycol mixture was distilled away until the temperature rose to 205 °C followed by refluxing for 3h. After cooling to room temperature, 50 ml of H₂O was added, the reaction extracted with ether and the extract dried with MgSO₄. The ether was removed and the product isolated by vacuum distillation. 23 g (56%) of **2e** was isolated: bp 140 °C/3 mm; ¹H NMR (60 MHz) δ 1.2-1.7 (m, 16 H), 2.5 (t, 4 H, J=6.5 Hz), 7.0 (s, 10 H).

1-Bromo-11-phenylundecane (7). Into a 250 ml flask, was added magnesium turnings (5.0 g, 0.21 mole) and THF (40 ml). 1,2-Dibromoethane (4.0 g) was added through a dropping funnel. After the vigorous reaction ceased, more THF (80 ml) was added into the flask. Subsequently, a solution of benzylchloride (12.6 g, 0.10 mole) in THF (20 ml) was added during 30 min. The mixture was allowed to stand for 2 h. Into 500 ml flask, 1,10-dibromodecane (30 g, 0.10 mole), THF (300 ml) and 0.1 M Li₂CuCl₄ solution (10 ml) were mixed and cooled with ice. The Grignard reagent solution was quickly transferred to a dropping funnel and added to the

mixture over a period of 3 h and stirred overnight. Methanol (10 ml) was added, the solvent was removed, and chloroform (250 ml) was added to dissolve the residue. The solution was washed with water and dried with magnesium sulfate. After removal of the solvent, the residue was distilled under reduced pressure to give 15.1 g (48.2%) of **7**: bp 135 °C/1mm; ¹H NMR (60 MHz) δ 1.2-1.9 (m, 18 H), 2.60 (t, 2 H, J=7 Hz), 3.36 (t, 2 H, J=6.5 Hz), 7.15 (s, 5 H).

1,22-Diphenyldocosane (2f). Sodium sand was made by heating sodium (3.54 g, 154 mmole) in dry xylene until molten, followed by shaking as the xylene cooled. Compound **7** (23.8 g, 77 mmole) was added in small portions to the reaction which was controlled by shaking and heating at short intervals. After all of the bromide (**7**) had been introduced, the mixture was let stand for 3 h. The excess sodium was destroyed by careful addition of ethanol, then water. The mixture was extracted with chloroform (3 x 50 ml). The chloroform solution was washed with water, dried, concentrated and recrystallized (ethanol) to give 7.12 g (40.2%) of **2f**: mp 58-59.5 °C; IR (KBr) 2916, 2846, 1469, cm⁻¹; ¹H NMR (60 MHz) δ 1.1-1.7 (m, 40 H), 2.5 (t, 4 H, J=7 Hz), 7.1 (s, 10H).

Bis[4-(chloroacetyl)phenyl] oxide (3a). The following is a modification of a published procedure.¹⁴ Finely ground AlCl₃ (50.0 g, 0.375 mol) was mixed with dichloromethane (50 ml) in a 250 ml flask and cooled to -10 °C. Chloroacetyl chloride (37.3 g, 0.33 mol) was added to the mixture as it was kept cool. Diphenyl ether (25.5 g, 0.15 mol) was dissolved in dichloromethane (10 ml) and charged to a dropping funnel. The diphenyl ether solution was added slowly dropwise to the mixture over 2 h while stirring and keeping the temperature below 0 °C. At the end of the addition, the mixture was left to warm to room temperature and stir overnight. The red colored solution was poured into a large quantity of ice (about 300 g). The organic layer was separated and the aqueous layer extracted with dichloromethane (50 ml) and the dichloromethane portions washed with water until neutral. The organic phase was then dried (magnesium sulfate), concentrated, recrystallized (ethanol), and dried to give 33.8 g (69.7%) of **3a**: mp 108-110 °C; ¹H NMR (60 MHz) δ 4.68 (s, 4 H), 7.0-7.3 (m, 4 H), 7.9-8.2 (m, 4 H).

Bis[4-(chloroacetyl)phenyl] sulfide (3b). A similar procedure described for the synthesis 3a was used except phenyl sulfide and chloroacetyl chloride were dissolved in dichloromethane and added to the AlCl_3 mixture. Phenyl sulfide (16.7 g, 0.090 mol), chloroacetyl chloride (30.6 g, 0.271 mol) and AlCl_3 (36.1 g, 0.271 mol) were used. The crude product (19 g, 62%) was decolorized by activated charcoal and recrystallized (acetone/ethanol) to give 10.9 g (35.7%) of 3b: mp 101.5-103 °C; ^1H NMR (60 MHz) δ 4.67 (s, 4 H), 7.4-7.6 (m, 4 H), 7.9-8.1 (m, 4 H).

Bis[4-(chloroacetyl)phenyl] triethylene glycol ether (3c). AlCl_3 (90.0 g, 0.675 mol) was mixed with dichloromethane (50 ml) and cooled to -10 °C. Chloroacetyl chloride (37.3 g, 0.33 mol) was added to the mixture and cooled to -10 °C. 2c (45.4 g, 0.15 mol) was dissolved in dichloromethane (30 ml) and slowly drop added to the mixture over 2 h. At the end of the addition, the mixture was heated to reflux and stirred overnight. The resulting mixture was worked up as described before. The crude product was recrystallized (THF), and dried to give 42.6 g (62.4%) of 3c: mp 89-91 °C; IR (KBr) 1689, 1600, 1261, 1219, 1184, cm^{-1} ; ^1H NMR (60 MHz) δ 3.75

(s, 4 H), 3.8-4.0 (m, 4 H); 4.1-4.3 (m, 4 H), 4.63 (s, 4 H), 6.8-7.1 (m, 4 H), 7.8-8.1 (m, 4 H).

Bis[4-(chloroacetyl)phenyl] methane (3d). 3d was prepared in 70.7% yield: mp 121-122 °C; IR (KBr) 1701, 1600, 1215 cm^{-1} ; ^1H NMR (60 MHz) δ 4.07 (s, 2 H), 4.63 (s, 4 H), 7.2-7.4 (m, 4 H), 7.8-8.0 (m, 4 H).

1,10-Bis[4-(chloroacetyl)phenyl] decane (3e). A 73.3% yield of 3e was obtained: mp 85-86 °C; IR (KBr) 2927, 2850, 1701, 1604, 1215, 817 cm^{-1} ; ^1H NMR (60 MHz) δ 1.2-1.7 (m, 16 H), 2.6 (t, 4 H, $J=6.5$ Hz), 4.53 (s, 4 H), 7.0-7.2 (m, 4 H), 7.6-7.8 (m, 4 H).

1,22-Bis[4-(chloroacetyl)phenyl]docosane (3f). 3f was prepared in 22.4% yield: mp 91-93 °C; IR (KBr) 2920, 2846, 1697, 1604, 1469, 1215, 1164, 995, 817, 790, 756, 721 cm^{-1} ; ^1H NMR (60 MHz) δ 1.1-1.7 (m, 40 H), 2.6 (t, 4 H), 4.6 (s, 4 H), 7.1-7.3 (m, 4 H), 7.7-7.9 (m, 4 H).

Bis[4-(O-ethylxanthateacetyl)phenyl] oxide (4a). A mixture of 3a (33.8 g, 0.105 mol) and O-ethylxanthic acid potassium salt (33.5 g, 0.209 mol) in acetone (450 ml) was heated to

reflux for 4h. The mixture was allowed to cool to room temperature and filtered. The precipitate was washed with dichloromethane (50 ml). The combined organic phase was concentrated to give crude **4a**. The crude **4a** was dissolved in dichloromethane (200 ml) and washed with water (2 x 200 ml). The solution was dried (magnesium sulfate), concentrated to give 47.2 g (91.4%) of **4a**: ^1H NMR (60 MHz) δ 1.44 (t, 6 H, $J=7\text{Hz}$), 4.73 (s, 4 H), 4.73 (q, 4 H, $J=7\text{Hz}$), 7.1-7.3 (m, 4 H), 8.0-8.3 (m, 4 H).

Bis[4-(O-ethylxanthateacetyl)phenyl] sulfide (4b). A 67% yield of **4b** was isolated after recrystallization from acetone/ethanol. ^1H NMR (60 MHz) δ 1.41 (t, 6 H, $J=7\text{ Hz}$), 4.67 (s, 4 H), 4.69 (q, 4 H, $J=7\text{Hz}$), 7.4-7.6 (m, 4 H), 8.0-8.2 (m, 4 H).

Bis[4-(O-ethylxanthateacetyl)phenyl] triethylene glycol ether (4c). A 88% yield of **4c** was isolated: IR (KBr) 1670, 1600, 1311, 1265, 1238, 1111, 1057 cm^{-1} ; ^1H NMR (60 MHz) δ 1.37 (t, 6 H, $J=7\text{Hz}$), 3.75 (s, 4 H), 3.8-4.0 (m, 4 H); 4.1-4.3 (m, 4 H), 4.58 (s, 4 H), 4.61 (q, 4 H, $J=7\text{Hz}$), 6.8-7.1 (m, 4 H), 7.8-8.1 (m, 4 H).

Bis[4-(O-ethylxanthateacetyl)phenyl] methane (4d). A 92.8% yield of **4d** was isolated. IR (KBr) 1681, 1600, 1226, 1114, 1053, 995 cm^{-1} ; ^1H NMR (60 MHz) δ 1.37 (t, 6 H, $J=7\text{ Hz}$), 4.07 (s, 2 H), 4.58 (q, 4 H, $J=7\text{ Hz}$), 4.60 (s, 4 H), 7.2-7.4 (m, 4 H), 7.8-8.0 (m, 4 H).

1,10-Bis[4-(O-ethylxanthateacetyl)phenyl] decane (4e). A 98.2% yield of **4e** was isolated. IR (KBr) 2916, 2850, 1693, 1604, 1219, 1057, 991, 817 cm^{-1} ; ^1H NMR (60 MHz) δ 1.2-1.7 (m, 22 H), 2.6 (t, 4 H, $J=6.5\text{ Hz}$), 4.5 (s, 4 H), 4.5 (q, 4 H, $J=7\text{ Hz}$), 7.0-7.2 (m, 4 H), 7.6-7.8 (m, 4 H).

1,22-Bis[4-(O-ethylxanthateacetyl)phenyl] docosane (4f). A 99% yield of **4f** was isolated. ^1H NMR (60 MHz) δ 1.1-1.7 (m, 40 H), 2.6 (t, 4 H, $J=7\text{ Hz}$), 4.6 (s, 4 H), 4.6 (q, 4 H, $J=7\text{ Hz}$), 7.1-7.3 (m, 4 H), 7.8-8.0 (m, 4 H).

Bis[4-(2-oxo-1,3-dithioly)phenyl] oxide (5a). A solution of **4a** (22.0 g, 44.5 mmol) in acetic acid (200 ml) was heated to reflux. A solution of 30% (by weight) HBr in acetic acid (120 ml) was added to the flask. During the addition, **5a** begin to precipitate out. The mixture was heated to reflux for 3h, allowed to cool to room temperature and filtered. The solid crude product

was dissolved in dichloromethane (200 ml) and washed with water until neutral. The solution was then dried (magnesium sulfate), concentrated, recrystallized (dichloromethane/acetone), and dried to give 12.5 g (69.8%) of **5a**: mp 146-148°C; IR (KBr) 1635, 1496, 1253, 871, cm^{-1} ; ^1H NMR (200 MHz) δ 6.77 (s, 2 H), 7.06 (m, 4 H), 7.42 (m, 4 H); ^{13}C NMR (50 MHz) δ 192.22, 157.31, 134.08, 128.31, 128.00, 119.52, 111.21. Anal. Calcd for $\text{C}_{18}\text{H}_{10}\text{O}_3\text{S}_4$: C, 53.71; H, 2.50; S, 31.86. Found: C, 53.53; H, 2.49; S, 31.22.

Bis[4-(2-oxo-1,3-dithioly)phenyl] sulfide (5b). The crude product was dissolved in dichloromethane, washed with water, decolorized by activated charcoal and filtered through a silica gel column. The elute was concentrated to give 32% of **5b**: mp 160-162 °C; IR (KBr) 1635, 1483, 1400, 875, 763 cm^{-1} ; ^1H NMR (300 MHz) δ 6.86 (s, 2 H), 7.37 (s, 8 H); ^{13}C NMR (75 MHz) δ 191.94, 136.60, 134.00, 131.68, 131.55, 127.07, 112.22. Anal. Calcd for $\text{C}_{18}\text{H}_{10}\text{O}_2\text{S}_5$: C, 51.65; H, 2.41. Found: C, 51.43; H, 2.36.

Bis[4-(2-oxo-1,3-dithioly)phenyl] triethylene glycol ether (5c). **4c** (8.5 g, 13.5 mmol) was dissolved in acetic acid (100 ml) and 30% HBr in acetic acid (50 ml). The mixture was heated to reflux for 20 min and then stirred overnight at room temperature. The crude product was purified as described for **5b** to give 0.9 g (12%) of **5c**: mp 125-126°C; IR (KBr) 1627, 1504, 1257, 1134, 871, 821, 775 cm^{-1} ; ^1H NMR (300 MHz) δ 3.75 (s, 4 H), 3.87 (t, 4 H, $J=4.5$ Hz), 4.14 (t, 4 H, $J=4.5$ Hz), 6.66 (s, 2 H), 6.90-6.93 (m, 4 H), 7.30-7.33 (m, 4 H); ^{13}C NMR (75 MHz) δ 192.63, 159.50, 134.65, 127.59, 125.58, 115.21, 109.79, 70.91, 69.66, 67.60. Anal. Calcd for $\text{C}_{24}\text{H}_{22}\text{O}_6\text{S}_4$: C, 53.91; H, 4.15. Found: C, 53.49; H, 3.93.

Bis[4-(2-oxo-1,3-dithioly)phenyl] methane (5d). An 84.5% yield of **5d** was isolated using the same procedure described for **5a**: mp 155-156 °C; IR (KBr) 1635, 864, 775 cm^{-1} ; ^1H NMR (300 MHz) δ 4.01 (s, 2 H), 6.79 (s, 2 H), 7.20-7.23 (m, 4 H), 7.34-7.37 (m, 4 H); ^{13}C NMR (75 MHz) δ 192.34, 141.68, 134.69, 130.93, 129.66, 126.58, 111.31, 41.22. Anal. Calcd for $\text{C}_{19}\text{H}_{12}\text{O}_2\text{S}_4$: C, 56.97; H, 3.02. Found: C, 56.51; H, 2.72.

1,10-Bis[4-(2-oxo-1,3-dithioly)phenyl] decane (5e). An 83.4% yield of **5e** was isolated using the same procedure described for **5a**: mp 123-124°C; IR (KBr) 2924, 2850, 1627, 1504, 871 cm^{-1} ; ^1H NMR (300 MHz) δ 1.28 (brs, 12 H), 1.60 (t, 4 H, $J=7.5$ Hz), 2.61 (t, 4 H, $J=7.5$ Hz), 6.77 (s, 2 H), 7.19-7.22 (m, 4 H), 7.31-7.34 (m, 4 H); ^{13}C NMR (75 MHz) δ 192.68, 144.38, 135.08, 130.11, 129.17, 126.20, 110.71, 35.62, 31.22, 29.48, 29.41, 29.19. Anal. Calcd for $\text{C}_{28}\text{H}_{30}\text{O}_2\text{S}_4$: C, 63.84; H, 5.74. Found: C, 63.89; H, 5.53.

1,22-Bis[4-(2-oxo-1,3-dithioly)phenyl] docosane (5f). A 32% yield of **5f** was isolated using the same procedure described for **5a**: mp 120-122°C; IR (KBr) 2920, 2846, 1631, 1504, 871 cm^{-1} ; ^1H NMR (300 MHz) δ 1.24-1.57 (m, 40 H), 2.61 (t, 4 H, $J=7.5$ Hz), 6.77 (s, 2 H), 7.19-7.22 (m, 4 H), 7.31-7.34 (m, 4 H); ^{13}C NMR (75 MHz) δ 192.64, 144.45, 135.15, 130.14, 129.19, 126.22, 110.67, 35.64, 31.23, 30.86, 29.66, 29.54, 29.43, 29.21. Anal. Calcd for $\text{C}_{40}\text{H}_{54}\text{O}_2\text{S}_4$: C, 69.12; H, 7.83. Found: C, 68.39; H, 7.35.

Bis[4-(1,2-dimethylthiolene)phenyl] oxide (8). A mixture of **5a** (0.100 g, 0.248 mmol) and sodium ethoxide (0.101 g, 1.49 mmol) in ethanol (15 ml) was heated at 60°C and stirred for 40 min. Iodomethane (0.353 g, 2.48 mmol) in ethanol (15 ml) was added to the mixture the resulting mixture cooled to room temperature, and the volatile materials removed by roto-evaporation. The residue was extracted with chloroform (20 ml) and filtered. The filtrate was concentrated to give 0.101 g (100%) of **8**: mp 103-105 °C; IR (KBr) 2997, 2916, 1489, 1249, 810 cm^{-1} ; ^1H NMR (300 MHz) δ 2.07 (s, 6 H), 2.40 (s, 6 H), 6.38 (s, 2 H), 6.94-6.97 (m, 4 H), 7.39-7.42 (m, 4 H); ^{13}C NMR (75 MHz) δ 156.42, 133.79, 131.42, 131.36, 128.64, 118.75, 17.46, 16.02. Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{OS}_4$: C, 59.08; H, 5.45; S, 31.54. Found (after recrystallization from $\text{Et}_2\text{O}/\text{C}_5\text{H}_{12}$): C, 59.26; H, 5.63; S, 31.15.

Poly[[1,1'-oxybis[4-(1,2-dithiolato)phenyl]benzene]] nickel (II) (11a). A mixture of **5a** (0.200 g, 0.497 mmol) and sodium ethoxide (0.203 g, 2.98 mmol) in ethanol (30 ml) was heated at 60°C with stirring for 40 min. Nickel bromide (0.109 g, 0.497 mmol) dissolved in ethanol (30 ml) was added to the mixture via cannula. The resulting mixture was heated at 60°C overnight and cooled to room temperature. Iodine (0.252 g, 0.994 mmol) was dissolved in ethanol (10 ml) and

added to the mixture. The resulting mixture was stirred for 2 h. The black polymer was collected by filtration and washed thoroughly with water and ethanol. The product was then dried under vacuum to give 0.170 g (84.4%) of polymer **11a**: IR (KBr) 1587, 1498, 1367, 1245, 1189, 1167, 857, 833, 798 cm^{-1} ; UV-Vis-NIR (DMF) λ_{max} (ϵ) 265 (48100), 310 (54700), 490 (sh, 2500), 930 (13200) nm. Anal. Calcd for $(\text{C}_{16}\text{H}_{10}\text{NiOS}_4)_n$: C, 47.43; H, 2.49; Ni, 14.49; S, 31.65. Found: C, 47.49; H, 2.91; Ni, 10.80; S, 33.49; I, 2.17; Br, 0.51.

Poly[[1,1'-thiobis[4-(1,2-dithiolatoethenyl)benzene]]nickel(II)] (11b). A 79.5% yield of polymer **11b** was isolated: IR (KBr) 1581, 1485, 1365, 1190, 1010, 861, 827, 797 cm^{-1} ; UV-Vis-NIR (DMF) λ_{max} (ϵ) 273 (19700), 316 (25300), 350 (sh, 18500), 500 (sh, 1100), 930 (5500) nm. Anal. Calcd for $(\text{C}_{16}\text{H}_{10}\text{NiS}_5)_n$: C, 45.62; H, 2.39. Found: C, 37.59; H, 2.69.

Poly[[1,1'-(triethylene glycol ether)-bis[4-(1,2-dithiolato-ethenyl)benzene]]nickel(II)] (11c). A mixture of **5c** (0.200 g, 0.374 mmol) and sodium ethoxide (0.153 g, 2.24 mmol) in ethanol (30 ml) was heated at 60°C with stirring for 1 h. Nickel bromide (0.082 g, 0.374 mmol) dissolved in ethanol (30 ml) was added to the mixture via cannula. The resulting mixture was heated at 60°C overnight and cooled to room temperature. The mixture was opened to air and stirred for 2 h. The black polymer was collected by filtration and washed thoroughly with water and ethanol, then dried under vacuum to give 0.182 g (90.5%) of polymer **11c**: IR (KBr) 1597, 1508, 1364, 1256, 1191, 1143, 1112, 862, 832 cm^{-1} ; UV-Vis-NIR (DMF) λ_{max} (ϵ) 265 (21100), 310 (16700), 500 (sh, 500), 935 (3100) nm. Anal. Calcd for $(\text{C}_{22}\text{H}_{22}\text{NiO}_4\text{S}_4)_n$: C, 49.17; H, 4.13. Found: C, 43.55; H, 3.82.

Poly[[1,1'-methane-bis[4-(1,2-dithiolatoethenyl)benzene]] nickel(II)] (11d). The procedure described for the synthesis of **11a** was followed. 0.180 g (89.5%) of polymer **11d** was isolated as a black powder: IR (KBr) 1599, 1369, 1191, 861, 781 cm^{-1} ; UV-Vis-NIR (DMF) λ_{max} 260, 310, 500, 930 nm. Anal. Calcd for $(\text{C}_{17}\text{H}_{12}\text{NiS}_4)_n$: C, 50.64; H, 3.00. Found: C, 49.20; H, 3.07.

Poly[[1,1'-decane-bis[4-(1,2-dithiolatoethenyl)benzene]] nickel(II)] (11e). The procedure described for the synthesis of **11c** was followed. 0.171 g (85.0%) of polymer **11e**

was isolated as a black powder: IR (KBr) 2924, 2850, 1604, 1369, 1323, 1192, 864, 833, 794 cm^{-1} ; UV-Vis-NIR (DMF) λ_{max} 260, 310, 490, 935 nm. Anal. Calcd for $(\text{C}_{26}\text{H}_{30}\text{NiS}_4)_n$: C, 58.98; H, 5.71. Found: C, 54.07; H, 5.35.

Poly[[1,1'-docosane-bis[4-(1,2-dithiolatoethenyl)benzene]] nickel (II)] (11f). The procedure described for the synthesis of **11c** was followed. An 81% yield of polymer **11f** was isolated as a black powder: IR (KBr) 2920, 2850, 1681, 1604, 1369, 1192, 864, 837, 794 cm^{-1} ; UV-Vis-NIR (DMF) λ_{max} 260, 310, 500, 930 nm. Anal. Calcd for $(\text{C}_{38}\text{H}_{54}\text{NiS}_4)_n$: C, 65.41; H, 7.80. Found: C, 64.77; H, 7.63.

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Table I. NIR Absorbance Results for Polymer 11c

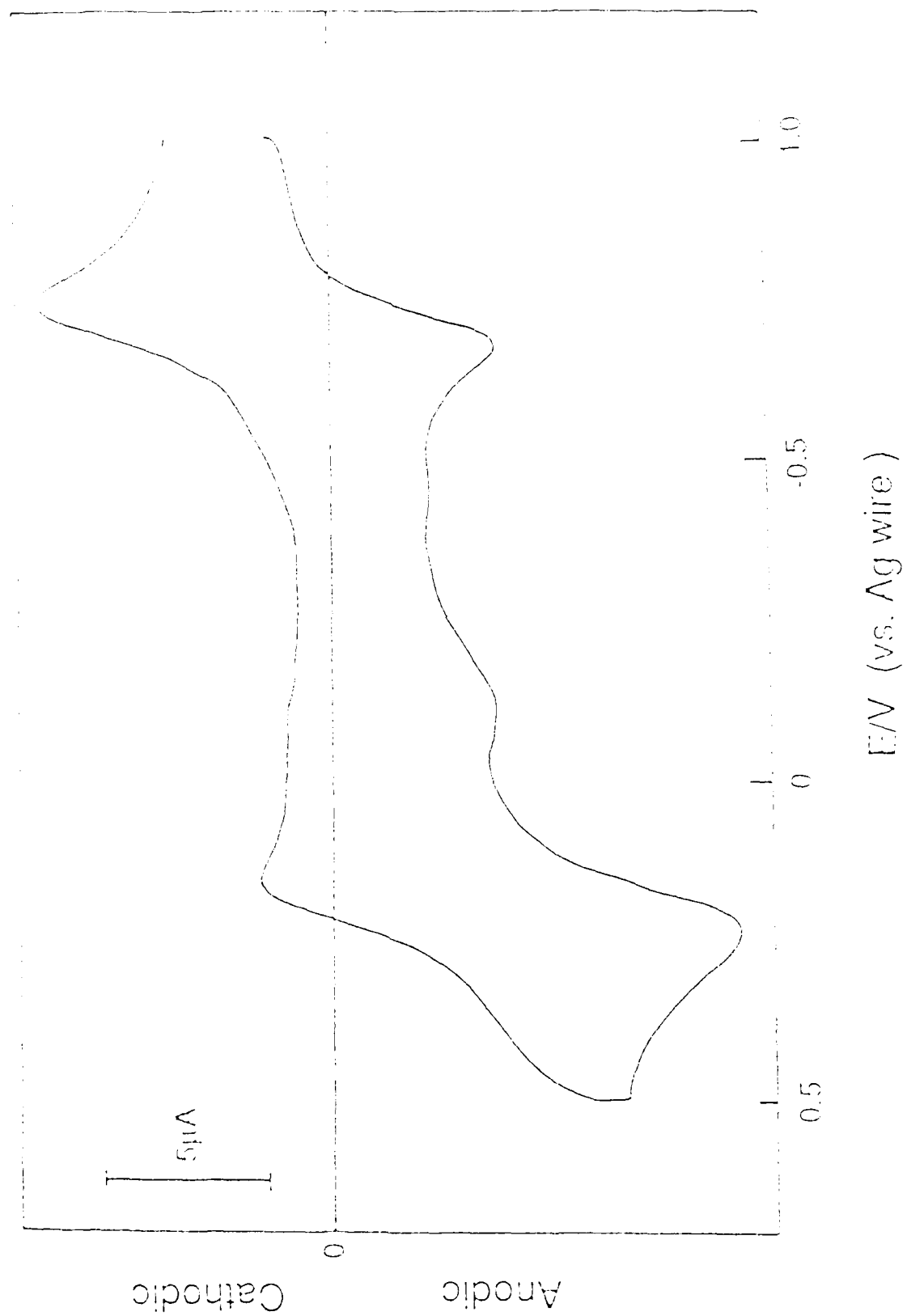
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THF	7.6	880
HMPA	30.0	927
DMF	36.7	935
DMSO	46.6	941

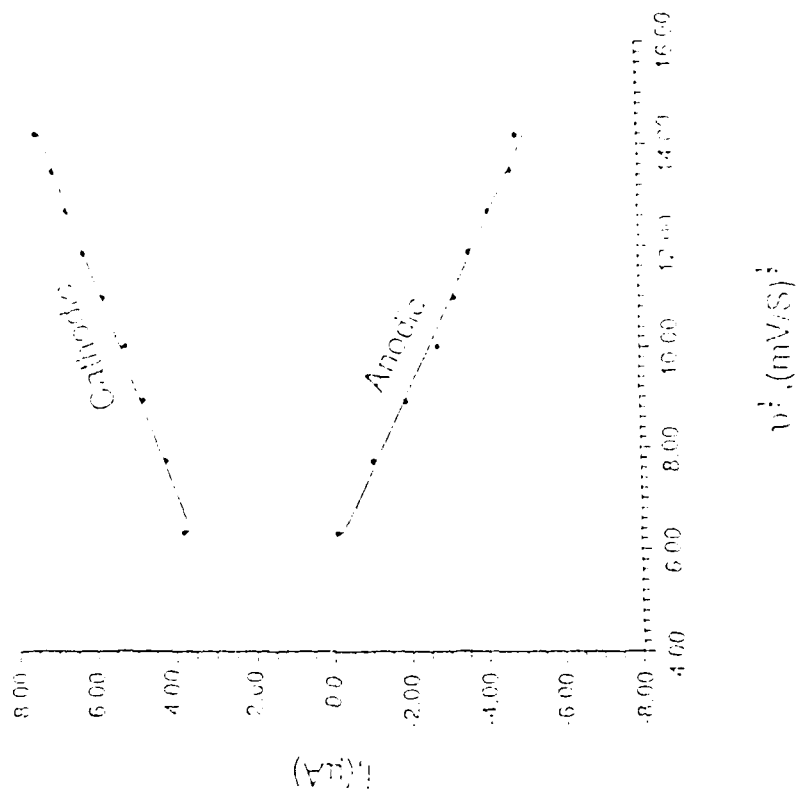
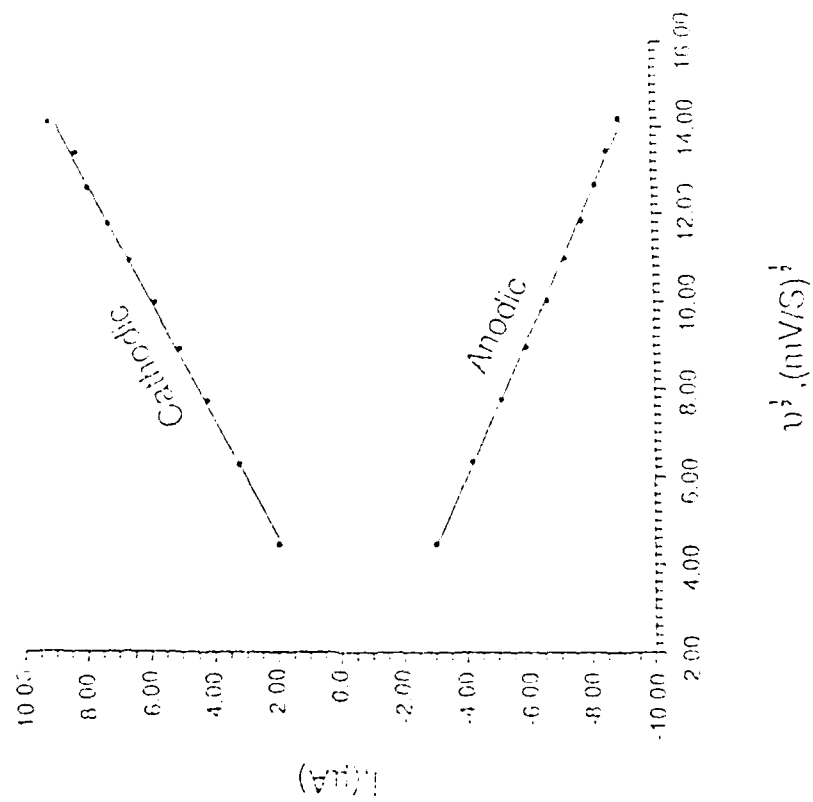
Figure Captions

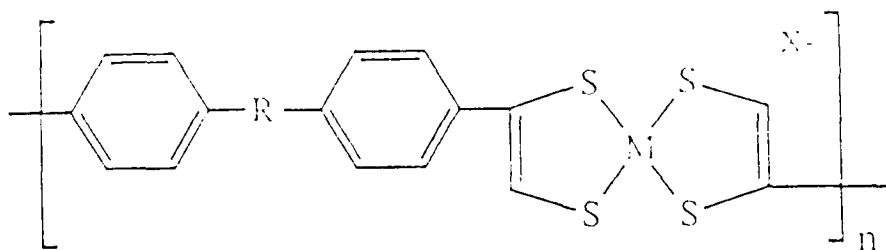
Figure 1. UV-VIS-NIR spectrum of polymer 11c.

Figure 2. Cyclic voltammogram for polymer 11c on a carbon button working electrode in a 0.1 M TBAClO₄/DMF solution. Potentials are reported versus a silver wire quasi-reference electrode.

Figure 3. Scan rate (ν) dependence of both anodic and cathodic peak current (i_p) for (a) $[\text{NiL}_2^{1+}]_n \rightleftharpoons [\text{NiL}_2^0]_n$ and (b) $[\text{NiL}_2^{2+}]_n \rightleftharpoons [\text{NiL}_2^{1+}]_n$.

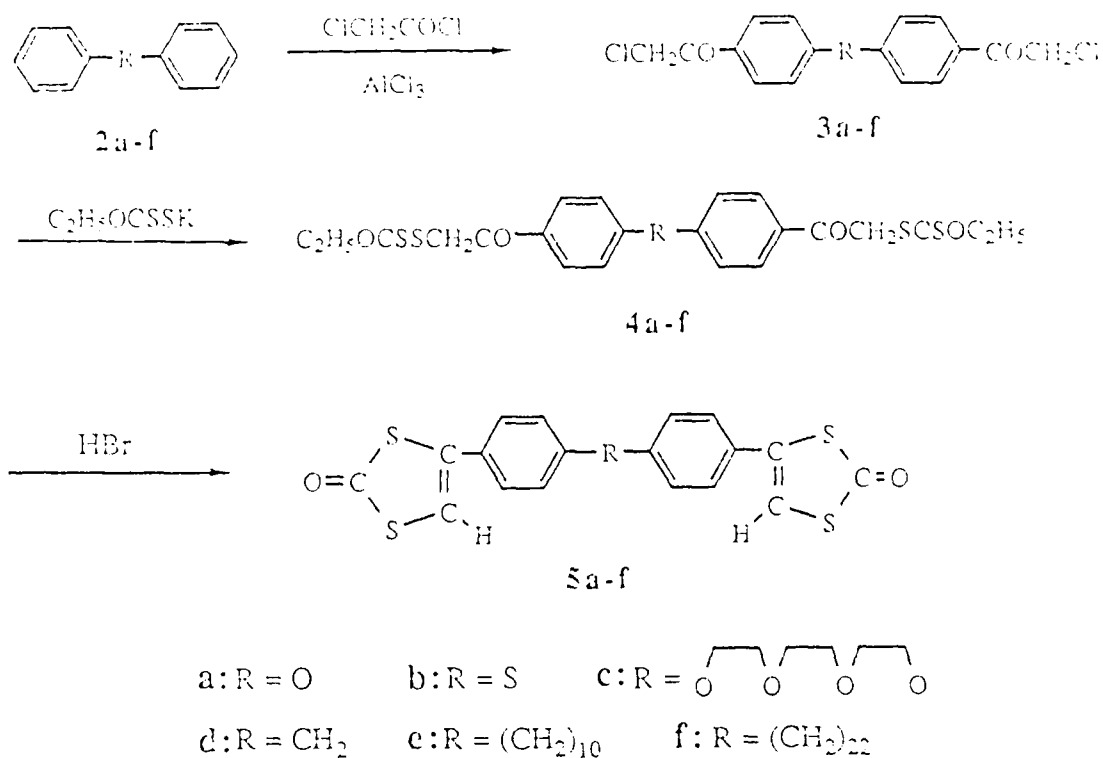




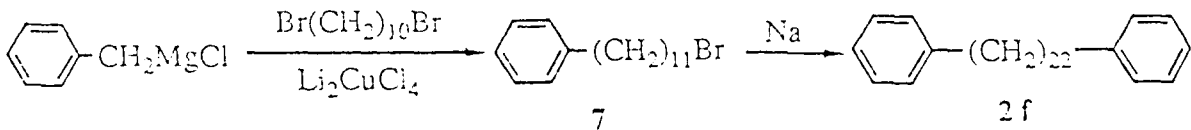
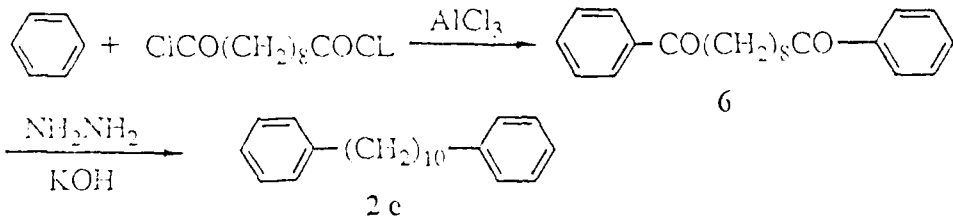
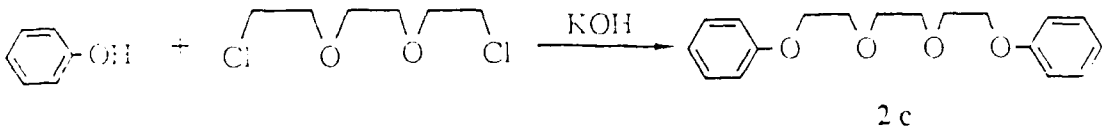


1

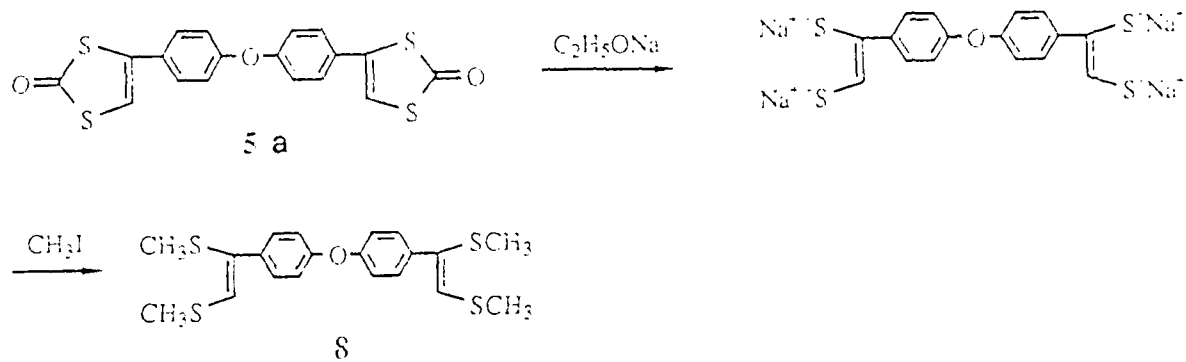
Scheme 1



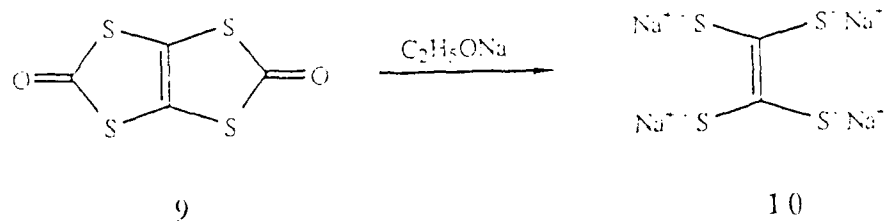
Scheme II



Scheme III



Scheme IV



4



Scheme VI

