

Synthesis and electrochemistry of new thienyl – Schiff base complexes¹

A. Pietrangelo, B.N. Boden, M.J. MacLachlan, and M.O. Wolf

Abstract: The synthesis and characterization of nickel(II), copper(II), and vanadyl ($[V=O]^{2+}$) complexes of two new thienyl-substituted Schiff base ligands are reported. Cyclic voltammetry of some of these complexes showed oxidation waves, but none of the complexes formed conductive polymer films upon repeated cycling. UV–vis absorption spectroscopy shows that some of the complexes exhibit enhanced conjugation, and the radical cations formed on these chromophores appear to be too stable to undergo oxidative coupling.

Key words: Schiff base, salphen, conjugated polymer, electrochemistry.

Résumé : On a effectué la synthèse et on a caractérisé les complexes du nickel(II), du cuivre(II) et du vanadyle ($[V=O]^{2+}$) de deux ligands dérivés de bases de Schiff substituées par de groupes thiényles. La voltampérométrie cyclique a permis de montrer que quelques-uns de ces complexes présentent des vagues d'oxydation, mais aucun de ces complexes ne forme de films de polymères conducteurs après des cycles voltampérométriques répétés. La spectroscopie d'absorption UV/vis montre que certains de ces complexes donnent lieu à une conjugaison exaltée et que les cations radicaux qui se forment sur ces chromophores semblent trop stables pour subir des couplages oxydants.

Mots-clés : base de Schiff, salphène, polymère conjugué, électrochimie.

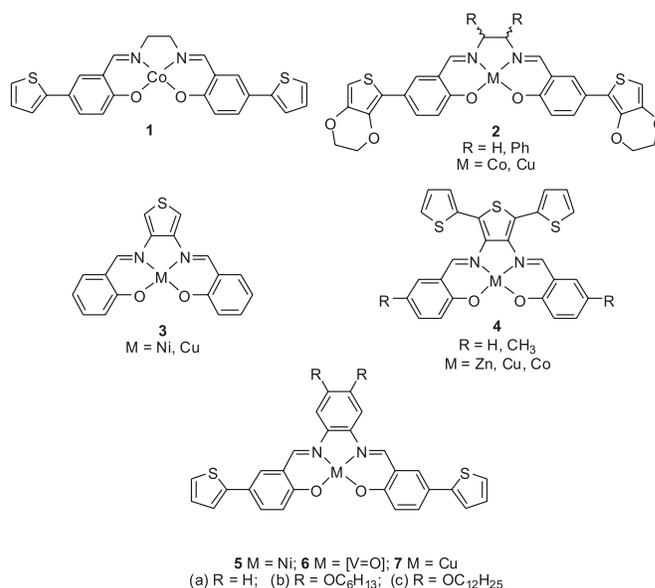
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Introduction

Conjugated polymers containing metal complexes are of interest because they combine the electronic properties of a highly delocalized π -system with the catalytic, magnetic, and optical properties of a metal (1). Schiff base complexes are a particularly intriguing class of metal complexes because they have large second-order and third-order NLO responses, are stable to over 300 °C, and have electronic or magnetic characteristics that permit additional functionality, such as chemical sensing, catalysis, and supramolecular organization (2–4). Both conjugated and non-conjugated polymers incorporating Schiff base complexes have been reported (5). Schiff base complexes containing a range of transition metals with pendant thiophene units have been electropolymerized to generate conductive polymer films that exhibit catalytic, sensing, and nonlinear optical properties (6).

The groups of both Swager and Reynolds have synthesized thiophene-containing Schiff base monomers and studied their electropolymerization. Oxidative coupling of monomers **1** and **2** ($M = Co$) gave conductive polymers where the metal does not contribute to conductivity but is necessary for electropolymerization (6b). Changing the substituents on **2** from

$R = H$ to larger groups such as $R = Ph$ increases interchain spacing resulting in a reduction in conductivity for Cu(II)-containing polymers (6c). Reynolds investigated electropolymerization of monomers **3** and **4**, and found that polymerization occurs at the phenylene group for **3** (6f, 6g). In the case of **4**, polymerization could occur at either the thienyl or phenylene ring, except when $R = CH_3$, in which case polymerization occurs exclusively through the oligothiophene moiety.



Received 21 April 2008. Accepted 24 July 2008. Published on the NRC Research Press Web site at canjchem.nrc.ca on 12 November 2008.

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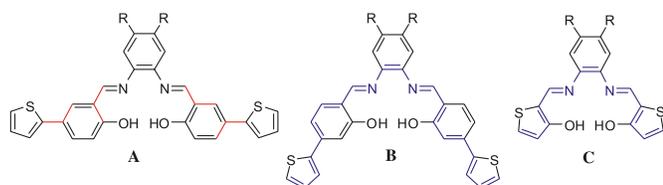
¹This article is part of a Special Issue dedicated to Professor R. Puddephatt.

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We recently reported the electropolymerization of substituted Schiff base complexes **5–7** in microgravity (6a). In some cases, improved film order was observed when film

growth occurred in the absence of gravity-driven convection currents as evidenced by higher χ^3 susceptibilities.

While electropolymerization is known for salphen complexes formed from 5-(2-thienyl)salicylaldehyde, such as **5**–**7**, it has not been studied for salphens made from 4-(2-thienyl)salicylaldehyde. In compounds with the general structure **A**, the relative meta arrangement between the thienyl and imine substituents on the phenyl ring leads to less effective conjugation than para arrangements (structure **B**). Visually it may be noted that the π -conjugation pathway between the thienyl substituents for **A** cannot be drawn with alternating single and double bonds in any important resonance structure, whereas in structure **B** the conjugation appears to be improved, inasmuch as this model is an indication of delocalization. Thus, we set out to probe whether 4-substituted structures polymerize and whether the resulting materials show significantly different electronic properties from those made from 5-substituted monomers.



Another possible approach to a fully conjugated monomer involves replacing the terminal phenyl rings with thiophene groups, as in structure **C**. Here, we report a series of new conjugated monomers, along with electrochemistry and electronic absorption data.

Results and discussion

Synthesis

To prepare 4-(2-thienyl)salicylaldehyde **9**, 4-iodosalicylaldehyde **8** was coupled to 2-tributylstannylthiophene via Stille coupling affording **9** as a beige product in 92% yield (Scheme 1). Schiff base condensation of **9** with diamine **10a** gave salphen **11a** as an orange solid. With longer alkoxy chains, a longer reaction time was required for complete conversion to the product (**11b** and **11c**). The ^1H NMR spectrum of **11b** shows an imine resonance at δ 8.56 and a hydroxyl resonance at δ 13.34 (Fig. 1).

Heating **11b** at reflux in THF with the appropriate metal salt yielded the salphen metal complexes **12b**–**14b**. All three metal complexes crystallized readily, but the resulting crystals were thin and unsuitable for single crystal X-ray diffraction studies. The ^1H NMR spectrum of the diamagnetic Ni(II) complex **12b** was consistent with its structure, and all three complexes gave satisfactory mass spectrometry data and elemental analysis.

Thienolphenylenediimine (thienphen) complexes **19a** and **19b** were prepared by the route shown in Scheme 2. 3-Methoxythiophene **16** was prepared by Cu(I)-catalyzed Ullmann-type coupling of sodium methoxide with 3-bromothiophene **15** (7). Ortho-directed lithiation followed by quenching with DMF yielded 2-formyl-3-methoxythiophene **17** after work-up (8). Deprotection with BBr_3 afforded air-sensitive 2-formyl-3-hydroxythiophene **18** (9). Condensation

Scheme 1.

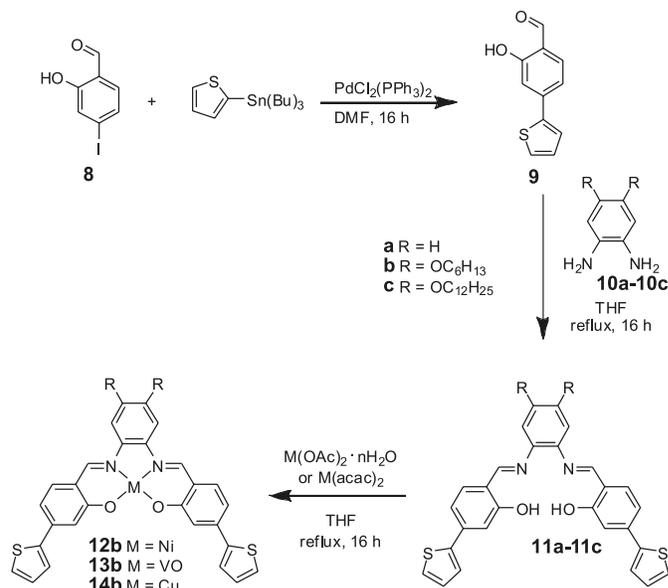
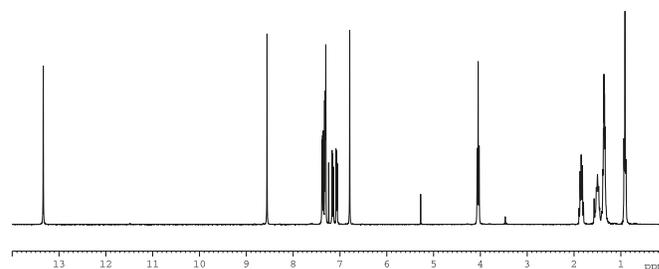
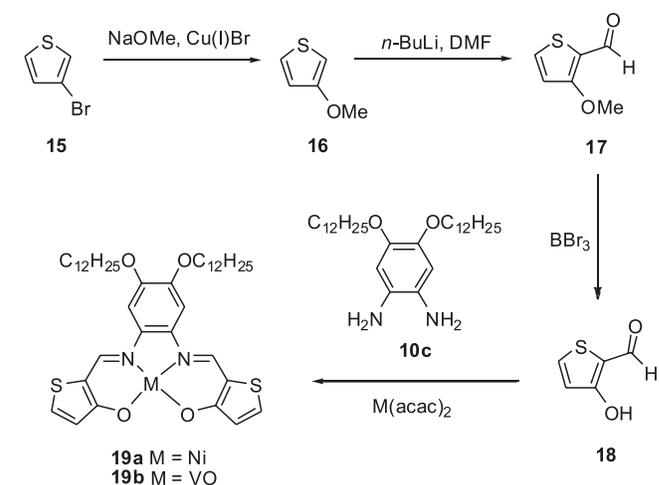


Fig. 1. ^1H NMR (300 MHz, CDCl_3) spectrum of **11b**.



Scheme 2.

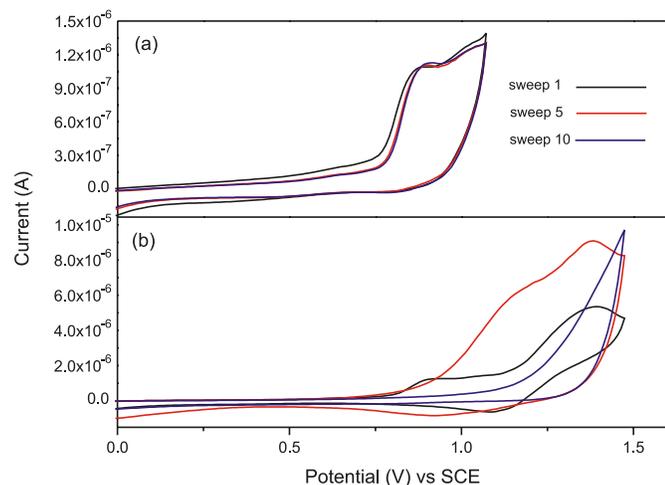


of **18** with diamine **10c** in the presence of a metal salt gave thienphen complexes **19a** and **19b** in 72% yield.

Electrochemistry

Electropolymerization of the three metal complexes **12b**–**14b** was attempted, but only the Ni(II) complex **12b** and Cu(II) complex **14b** showed oxidation waves within the solvent window. Repeated cycling through the first oxidation

Fig. 2. Cyclic voltammetry of **14b**. (a) 10 scans to 1.0 V. (b) 10 scans to 1.4 V. Only scans 1, 5 and 10 are shown. Pt-disc working electrode, 0.1 mol/L $[n\text{-Bu}_4\text{N}]\text{PF}_6$ in CH_2Cl_2 , 100 mV/s scan rate.



wave (~ 1 V vs. SCE) for both compounds resulted in identical cyclic voltammograms (CVs) on each sweep (Fig. 2a). No film growth was visible on either Pt-disc or gold-on-glass working electrodes. Cycling through both the first and second oxidation waves (1.4 V vs. SCE) resulted in significant changes in sequential CVs (Fig. 2b). An increase in current and positive shift of the oxidation wave was observed, along with the formation of a red film on the electrode surface. CVs of these films showed no oxidation or reduction features in the solvent window.

To explain these results, we consider the radical cations expected to form upon one electron oxidation of the dithienylsalphen monomers (Fig. 3). The radical cation in the oxidized species **A**⁺ is more delocalized than in the oxidized species **B**⁺; as a result, the radical cation of **B** may be stable enough to prevent polymerization. This explains the lack of polymerization observed when scanning only to the first oxidation wave in **12b** and **14b**. There are no known examples of electropolymerization of thiophene-substituted benzene with an imine para to the thienyl group. Upon scanning to higher potentials, a redox-inactive film is formed. The cyclic voltammetry differs from that observed upon electropolymerization of **5–7** where a lower potential feature attributed to reversible oxidation of the polymer backbone is observed. It is possible that at high potentials monomers **12b** and **14b** undergo coupling at the alkoxy substituted phenyl rings as has been observed previously in related species prepared by Reynolds and coworkers (6f, 6g).

Cyclic voltammetry of **19a** (Fig. 4) shows a quasi-reversible wave at 0.7 V vs. SCE, as well as two higher-potential irreversible waves. These waves are attributed to oxidation of the metal centre as well as ligand-based oxidations. No sign of electropolymerization is observed with repeated scanning to potentials up to 2.0 V. Complex **19b** also does not electropolymerize and shows an anodic wave at 0.9 V vs. SCE with a large associated cathodic wave. It is possible that the oxidized species generated here are also stabilized via resonance stabilization of the radical cations (Fig. 5).

Fig. 3. Formation of the radical cations of **A** and **B**, showing one resonance structure for each monomer.

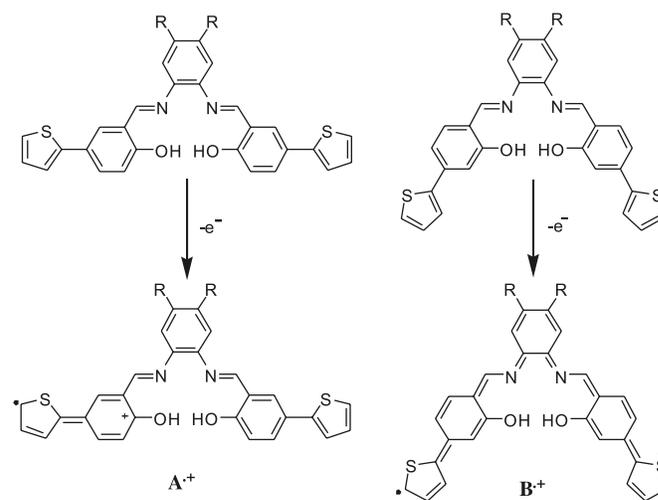
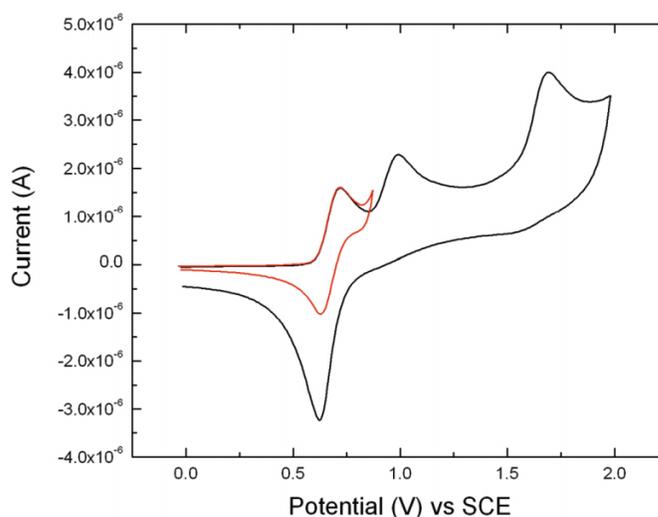


Fig. 4. Cyclic voltammetry of **19a**. The red trace (light trace in print version) shows scan reversal after the first oxidation wave; the black trace (heavy) shows a scan to 2 V. Pt-disc working electrode, 0.1 mol/L $[n\text{-Bu}_4\text{N}]\text{PF}_6$ in CH_2Cl_2 , 100 mV/s scan rate.



The electronic absorption spectra of the monomers can be used to provide insight into the degree of conjugation, because increased conjugation is expected to result in a bathochromic shift. The spectra for complexes **12b–14b** are shown in Fig. 6. At higher energy, the spectrum is dominated by peaks associated with the ligand (e.g., $\pi\text{-}\pi^*$ transitions) whereas the lower energy peaks are attributed to $n\text{-}\pi^*$ and metal-based transitions (metal to ligand charge transfer bands, $d\text{-}d$ transitions). Comparison of UV-vis spectra of the 5-substituted monomers (**5–7**) with the corresponding 4-substituted species (**12b–14b**) reveals that, as expected, the low energy charge transfer absorption bands are shifted only slightly. The higher energy bands, on the other hand, are consistently shifted to lower energy in the 4-substituted monomers (cf. 320 nm for **5b** vs 350 nm for **12b**). These bands, attributed to $\pi\text{-}\pi^*$ transitions on the conjugated back-

Fig. 5. Formation of the radical cations of **19** (metal-based oxidation is not considered).

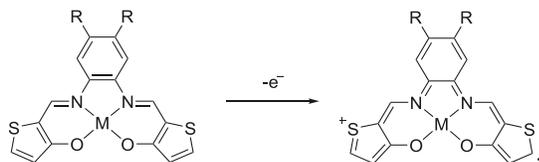
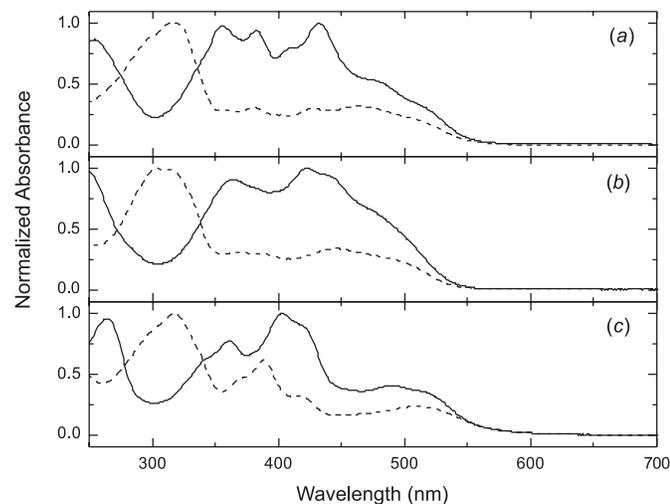


Fig. 6. Normalized absorption spectra of dithienylsalphen monomers in DCM (concentration $4.0 - 5.0 \times 10^{-6}$ mol/L), where (a) **5b** (----), **12b** (—); (b) **6b** (----), **13b** (—); (c) **7b** (----), **14b** (—).



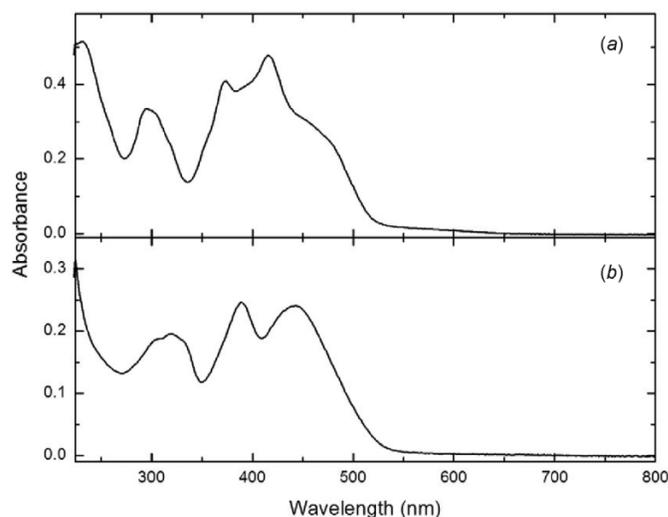
bone, shift in a manner consistent with enhanced conjugation.

The absorption spectra of **19a** and **19b** both have a higher energy band (~ 300 nm) attributed to the $\pi-\pi^*$ transition of the conjugated system (Fig. 7). This absorption is close in energy to the $\pi-\pi^*$ transition in **5b** and **6b** suggesting a similar extent of conjugation in these complexes. It is reasonable to conclude, based on these observations, that the conjugation is localized primarily over the diarylimine unit, regardless of whether the terminal aryl group is a substituted benzene or thiophene. The lower energy transitions in the spectra of **19a** and **19b** are attributed to CT transitions. The intensity of these transitions is comparable to the $\pi-\pi^*$ transition, possibly owing to an increase in the transition dipole moments as has been previously observed in similar complexes (10).

Conclusions

Two strategies for exploring the factors important in controlling electropolymerization of salphen complexes are reported. Extending the conjugation via substitution of the terminal phenyl ring at the 4-position with a thiophene group leads to a red-shift in the absorption spectrum, but results in species that do not electropolymerize. This is attributed to

Fig. 7. Absorption spectra of monomers in DCM (a) **19a** and (b) **19b**.



enhanced stabilization of the oxidized species owing to the extended conjugation. Similar observations were made for the thienolphenylenediimine complexes, and were also attributed to enhanced resonance stabilization of the oxidized species. Zotti has previously demonstrated that alkoxy-substituted hexathiophene oligomers do not polymerize well because of stabilization of the radical cation by the substituents (11). These results demonstrate that in order for electropolymerization to occur, the oxidized species cannot be too stable or the desired coupling reaction will not occur. The irreversibility of the oxidation waves associated with the organic groups suggests that other decomposition pathways may be available for the oxidized species. These results will guide future development of polymerizable thienyl – Schiff base complexes.

Experimental³

Compounds **8** (12) and **10a–10c** (13) were prepared according to literature procedures. Tetrahydrofuran (THF) was distilled over Na and benzophenone under N_2 . All other chemicals were purchased from Sigma-Aldrich, TCI, or Fisher and used as received. All reactions were carried out under nitrogen unless otherwise noted. UV–vis spectra were obtained on a Varian Cary 5000 UV–vis NIR spectrometer using a 1 cm cuvette. Infrared spectra were obtained using KBr discs or on NaCl plates with a Bomem MB-100 spectrometer or a Nicolet 4700 FTIR spectrometer. 1H NMR (300 or 400 MHz) and ^{13}C NMR (75.5 or 100.7 MHz) spectra were recorded on Bruker Avance 300 or Bruker Avance 400 spectrometers and were referenced internally to residual protonated solvent. Electrospray ionization (ESI) mass spectra were obtained on a Micromass LCT time-of-flight (TOF) mass spectrometer equipped with an electrospray ion source. Samples were analyzed in methanol–dichloromethane at 1 μ mol/L. EI spectra were obtained with a double focusing

³Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 3839. For more information on obtaining material refer to cisti-icist.nrc-cnrc.gc.ca/cms/unpub_e.shtml.

mass spectrometer (Kratos MS-50) coupled with a MASPEC data system with EI operating conditions of: source temperatures 120–220 °C and ionization energy 70 eV. Elemental analyses were obtained at the Microanalytical facility at the University of British Columbia. Melting points were recorded on a Fisher John's melting point apparatus.

Synthesis of 4-(2-thienyl)salicylaldehyde **9**

A solution of 2-tributylstannylthiophene (8.0 mL, 25.2 mmol) in DMF (40 mL) was added to a mixture of 4-iodosalicylaldehyde **8** (4.095 g, 16.5 mmol) and trans-dichlorobis(triphenylphosphine) palladium (II) (0.606 g, 0.863 mmol). After heating for 16 h, the reaction solution was diluted with ether (100 mL) and washed with aqueous ammonium chloride (3 × 150 mL). The organic layer was filtered through silica and the solvent was removed under vacuum to obtain a beige solid, which was washed with hexanes and filtered to yield 3.088 g (0.794 mmol, 92%) of product; mp 92–94 °C. UV-vis (CH₂Cl₂, nm (L mol⁻¹cm⁻¹)): λ_{max} (ε): 331 (2.7 × 10⁴). IR (KBr, cm⁻¹): 3098, 3074, 2834, 2748, 1650, 1625, 1557, 1529, 1492, 1431, 1312, 1235, 1207, 1184, 995, 852, 800, 694. ¹H NMR (400 MHz, CDCl₃) δ: 11.12 (s, 1H, OH), 9.84 (s, 1H, CHO), 7.53 (d, 1H, *J* = 8.1 Hz, aromatic CH), 7.45 (d, 1H, *J* = 3.9 Hz, aromatic CH), 7.40 (d, 1H, *J* = 4.8 Hz, aromatic CH), 7.25 (dd, 1H, *J*₁ = 8.1 Hz, *J*₂ = 1.5 Hz, aromatic CH), 7.21 (s, 1H, aromatic CH), 7.11 (dd, 1H, *J*₁ = 4.8 Hz, *J*₂ = 3.9 Hz, aromatic CH). ¹³C NMR (75.5 MHz, CDCl₃) δ: 195.7, 162.3, 142.7, 142.6, 134.5, 128.7, 127.7, 125.9, 119.8, 117.6, 114.1. ESI-MS *m/z*: 227 ([M + Na]⁺). Anal. calcd. for C₁₁H₈O₂S: C 64.69, H 3.95; found C 64.30, H 3.99.

Synthesis of *N,N'*-Phenylenebis(4-(2-thienyl)salicylideneimine) **11b**

1,2-Dihexyloxy-4,5-diaminobenzene **10b** (0.297 g, 0.962 mmol) and 4-thienylsalicylaldehyde **9** (0.486 g, 2.37 mmol) were combined in a 100 mL Schlenk flask under nitrogen. To this mixture was added 20 mL of dry THF to form an orange solution. The solution was heated to reflux overnight and was cooled to room temperature, after which the volume of solution was reduced. Addition of methanol to the solution caused precipitation of an orange solid, which was collected on a Büchner funnel and washed with additional methanol. Yield: 0.587 g, 0.86 mmol, 89%. Compounds **11a** and **11c** were synthesized in an analogous fashion using **10a** and **10c** with yields of 0.355 g (0.66 mmol, 77%) and 0.525 g (0.61 mmol, 66%), respectively.

11a

¹H NMR (400 MHz, CDCl₃) δ: 13.21 (s, 2H, OH), 8.62 (s, 2H, HC=N), 7.39 (dd, 2H, *J*₁ = 3.7 Hz, *J*₂ = 1.0 Hz, aromatic CH), 7.36 (d, 2H, *J* = 8.0 Hz, aromatic CH), 7.35–7.32 (m, 6H, aromatic CH), 7.25 (m, 2H, aromatic CH), 7.17 (dd, 2H, *J*₁ = 8.0 Hz, *J*₂ = 1.7 Hz, aromatic CH), 7.08 (dd, 2H, *J*₁ = 5.0 Hz, *J*₂ = 3.7 Hz, aromatic CH). ¹³C NMR (100.7 MHz, CDCl₃) δ: 162.9, 162.0, 143.6, 142.6, 139.3, 133.1, 128.4, 128.0, 126.5, 124.8, 119.8, 118.6, 116.9, 114.5. EI-MS: *m/z* = 480 (M⁺). HRMS calcd for C₂₈H₂₀N₂O₂S₂: 480.09662; found: 480.09674.

11b

mp 176–178 °C. UV-vis (CH₂Cl₂, nm (L mol⁻¹cm⁻¹)) λ_{max} (ε): 360 (5.0 × 10⁴). IR (KBr, cm⁻¹): 2950, 2928, 2853, 1608, 1510, 1375, 1263, 1189, 850, 804, 695. ¹H NMR (300 MHz, CDCl₃) δ: 13.34 (s, 2H, OH), 8.56 (s, 2H, HC=N), 7.39 (dd, 2H, *J*₁ = 3.7 Hz, *J*₂ = 0.9 Hz, aromatic CH), 7.35 (d, 2H, *J* = 8.0 Hz, aromatic CH), 7.32 (m, 4H, aromatic CH), 7.16 (dd, 2H, *J*₁ = 8.0 Hz, *J*₂ = 1.7 Hz, aromatic CH), 7.08 (dd, 2H, *J*₁ = 5.0 Hz, *J*₂ = 3.7 Hz, aromatic CH), 6.79 (s, 2H, aromatic CH), 4.05 (t, 4H, OCH₂), 1.86–0.88 (m, 22H, hexyl chain). ¹³C NMR (75.5 MHz, CDCl₃) δ: 161.7, 161.1, 149.3, 143.7, 138.7, 135.6, 132.7, 128.4, 126.3, 124.6, 118.8, 116.8, 114.3, 105.0, 70.0, 31.8, 29.5, 25.9, 22.8, 14.2. ESI-MS *m/z*: 681 ([M + H]⁺). Anal. calcd. for C₄₀H₄₄N₂O₄S₂: C 70.56, N 4.11, H 6.51; found C 70.36, N 4.43, H 6.43.

11c

¹H NMR (400 MHz, CDCl₃) δ: 13.31 (s, 2H, OH), 8.58 (s, 2H, HC=N), 7.39 (d, 2H, *J* = 3.7 Hz, aromatic CH), 7.35 (d, 2H, *J* = 8.0 Hz, aromatic CH), 7.32 (m, 4H, aromatic CH), 7.17 (dd, 2H, *J*₁ = 8.0 Hz, *J*₂ = 1.6 Hz, aromatic CH), 7.08 (dd, 2H, *J* = 5.0 Hz, *J* = 3.7 Hz, aromatic CH), 6.81 (s, 2H, aromatic CH), 4.06 (t, 4H, OCH₂), 1.86–0.88 (m, 46H, dodecyl chain). ¹³C NMR (100.7 MHz, CDCl₃) δ: 161.7, 161.0, 149.4, 143.6, 139.1, 135.2, 133.0, 128.4, 126.4, 124.7, 118.6, 116.9, 114.4, 105.0, 70.1, 32.2, 29.9, 29.9, 29.7, 29.6, 29.5, 26.3, 22.9, 14.3. EI-MS *m/z*: 848 (M⁺). HRMS calcd. for C₅₂H₆₈N₂O₄S₂: 848.46205; found: 848.46226.

11b

To a mixture of **11b** (0.137 g, 0.201 mmol) and nickel(II) acetate tetrahydrate (0.226 g, 0.908 mmol) was added 10 mL of distilled THF. The red solution was heated to reflux for 16 h. After cooling, MeOH was added to precipitate a red solid, which was subsequently filtered and washed with MeOH and petroleum ether. Yield: 0.095 g, 0.13 mmol, 64%; mp > 300 °C. UV-vis (CH₂Cl₂, nm (L mol⁻¹cm⁻¹)) λ_{max} (ε): 361 (4.3 × 10⁴), 403 (5.6 × 10⁴), 489 (2.2 × 10⁴). IR (KBr, cm⁻¹): 2953, 2930, 2859, 1607, 1584, 1501, 1475, 1438, 1362, 1282, 1188, 699. ¹H NMR (400 MHz, CDCl₃) δ: 7.87 (s, 2H, HC=N), 7.43 (s, 2H, aromatic CH), 7.39 (d, 2H, *J* = 3.4 Hz, aromatic CH), 7.32 (d, 2H, *J* = 5.0 Hz, aromatic CH), 7.26 (d, 2H, *J* = 8.3 Hz, aromatic CH), 7.07 (m, 2H, aromatic CH), 7.02 (s, 2H, aromatic CH), 6.88 (d, 2H, *J* = 8.3 Hz, aromatic CH), 3.97 (t, 4H, OCH₂), 1.81–0.88 (m, 22H, hexyl chain). ¹³C NMR (75.5 MHz, CDCl₃) δ: 165.4, 151.4, 149.7, 144.0, 139.9, 136.3, 133.7, 128.4, 126.4, 124.8, 119.7, 117.9, 114.1, 98.8, 64.2, 31.9, 29.4, 25.9, 22.8, 14.3. ESI-MS *m/z*: 759 ([M + Na]⁺). Anal. calcd. for C₄₀H₄₂N₂O₄S₂Ni: C 65.13, H 5.74; found C 65.16, H 5.82.

11b

To a mixture of **11b** (0.166 g, 0.244 mmol) and vanadyl acetylacetonate (0.191 g, 0.720 mmol) was added 10 mL of distilled THF. The red solution was heated to reflux for 16 h. After cooling, the volume of the solution was reduced and MeOH was added to precipitate a red-brown solid. The product was subsequently filtered and washed with MeOH

and petroleum ether. Yield: 0.136 g, 0.18 mmol, 75%; mp 293 °C (dec.). UV-vis (CH_2Cl_2 , nm ($\text{L mol}^{-1}\text{cm}^{-1}$)) λ_{max} (ϵ): 364 (4.6×10^4), 422 (5.0×10^4). IR (KBr, cm^{-1}) ν : 2956, 2927, 2857, 1604, 1577, 1509, 1479, 1430, 1377, 1275, 1191, 980, 696. ESI-MS m/z : 768 ($[\text{M} + \text{Na}]^+$). Anal. calcd. for $\mathbf{13b} \cdot \text{H}_2\text{O}$ ($\text{C}_{40}\text{H}_{44}\text{N}_2\text{O}_6\text{S}_2\text{V}$): C 62.89, H 5.81, N 3.67; found C 63.09, H 5.87, N 3.91.

14b

To a mixture of $\mathbf{11b}$ (0.158 g, 0.232 mmol) and copper(II) acetylacetonate (0.186 g, 0.710 mmol) was added 20 mL of distilled THF. The brown solution was heated to reflux for 16 h. After cooling, the solution was reduced and MeOH was added to precipitate the product. Subsequent filtration afforded a red solid which was washed with MeOH and petroleum ether. The product was recrystallized from DCM and MeOH. Yield: 0.118 g, 0.16 mmol, 69%; mp > 300 °C. UV-vis (CH_2Cl_2 , nm ($\text{L mol}^{-1}\text{cm}^{-1}$)) λ_{max} (ϵ): 356 (4.2×10^4), 383 (4.0×10^4), 432 (4.3×10^4). IR (KBr, cm^{-1}) ν : 2952, 2925, 2856, 1608, 1587, 1500, 1474, 1374, 1275, 1187, 696. MALDI-TOF-MS m/z : 742 (M^+). Anal. calcd. for $\text{C}_{40}\text{H}_{42}\text{N}_2\text{O}_4\text{S}_2\text{Cu}$: C 64.71, H 5.70, N 3.77; found C 64.99, H 5.80, N 4.00.

19a

Under a nitrogen atmosphere, 3-hydroxy-2-formylthiophene $\mathbf{18}$ (200 mg, 1.56 mmol), 4,5-didodecyloxy-1,2-phenylenediamine $\mathbf{10c}$ (300 mg, 0.629 mmol), and nickel acetylacetonate tetrahydrate (232 mg, 0.932 mmol) were dissolved in anhydrous THF (40 mL) and heated to reflux for 48 h. The red solution was then cooled to room temperature and concentrated under vacuum. Addition of methanol to the solution precipitated a red solid, which was collected by centrifugation, then washed with methanol. The product was a red solid (300 mg, yield 63%); mp > 210 °C. UV-vis (CH_2Cl_2 , nm ($\text{L mol}^{-1}\text{cm}^{-1}$)) λ_{max} (ϵ): 231 (27000), 295 (17500), 373 (21500), 416 (25000). IR (cm^{-1}) ν : 2918, 2850, 1600, 1571, 1518, 1487, 1469, 1443, 1338, 1281, 1190, 1142, 1076, 1041, 1032, 918, 812, 759, 698, 669, 593, 534, 466. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 7.81 (2H, s, aromatic CH), 7.40 (2H, d, $J = 5.7$ Hz, aromatic CH), 6.97 (2H, s, aromatic CH), 6.58 (2H, d, $J = 5.5$ Hz, aromatic CH), 3.84 (4H, t, $J = 6.7$ Hz, OCH_2), 1.65 (4H, m, CH_2), 1.11 (36H, m, CH_2), 0.71 (6H, t, $J = 6.8$ Hz, CH_3). EI-MS m/z : 752 (M^+ , 100%). Anal. calcd. for $\text{C}_{40}\text{H}_{58}\text{S}_2\text{N}_2\text{O}_4\text{Ni}$: C 63.74, H 7.76, N 3.72; found: C 63.35, H 7.90, N 4.08.

19b

The same procedure was used as for the preparation of $\mathbf{19a}$. The product was isolated as a red solid, yield 72%; mp > 210 °C. UV-vis (CH_2Cl_2 , nm ($\text{L mol}^{-1}\text{cm}^{-1}$)) λ_{max} (ϵ): 320 (14000), 388 (18000), 444 (17700). IR (cm^{-1}) ν : 2917, 2849, 1600, 1566, 1521, 1487, 1436, 1401, 1338, 1260, 1216, 1081, 1032, 982, 950, 796, 764, 720, 697, 681, 526, 489, 459. EI-MS m/z : 761 (M^+ , 100%). Anal. calcd. for $\text{C}_{40}\text{H}_{58}\text{N}_2\text{O}_5\text{S}_2\text{V}$: C 63.05, H 7.67, N 3.68; found: C 62.89, H 7.74, N 3.95.

Electrochemistry

Cyclic voltammetry experiments were conducted using either a Pine AFCBP1 or Autolab potentiostat. The working

electrode was a Pt disk, an indium tin oxide (ITO) thin film on glass, or Au (1000 Å) deposited on Si using a Cr (50 Å) adhesion layer. The counter electrode was a Pt mesh and the reference electrode a silver wire. An internal reference (decamethylferrocene) was added to correct the measured potentials with respect to saturated calomel electrode (SCE). $[(n\text{-Bu})_4\text{N}]\text{PF}_6$ was used as a supporting electrolyte and was purified by triple recrystallization from ethanol and dried at 90 °C under vacuum for 3 days. Dichloromethane used for CV was purified by passing the solvent through an activated alumina tower. Polymerizations were carried out in a solution containing 0.1 mol/L electrolyte, and 1 mM monomer. Polymers were grown by cycling a potential between 0 V and the onset of monomer oxidation (= 1.6 V) for a total of 10 cycles, at a scan rate of 100 mV/s.

Acknowledgement

We thank the Canadian Space Agency (CSA) and Natural Sciences and Engineering Research Council of Canada (NSERC) for funding. We thank Dr. Bryan Sih for cyclic voltammetry measurements.

References

- (a) M.O. Wolf. *Adv. Mater.* **13**, 545 (2001); (b) R.P. Kingsborough and T.M. Swager. *Prog. Inorg. Chem.* **48**, 123 (1999); (c) M.J. MacLachlan. *Frontiers in Transition Metal-Containing Polymers. Edited by A. Abd-El-Aziz and I. Manners.* John Wiley and Sons, Hoboken, NJ, 2007.
- (a) P.G. Cozzi. *Chem. Soc. Rev.* **33**, 410 (2004); (b) P. Guerriero, S. Tamburini and P. A. Vigato. *Coord. Chem. Rev.* **139**, 17 (1995).
- (a) P.G. Lacroix. *Eur. J. Inorg. Chem.* 339 (2001); (b) P.G. Lacroix, S. Di Bella, and I. Ledoux. *Chem. Mater.* **8**, 541 (1996).
- For recent examples, see: (a) X. Lu, W.-Y. Wong, and W.-K. Wong. *Eur. J. Inorg. Chem.* 523 (2008); (b) S. Manivannan, R. Prabhakaran, K.P. Balasubramanian, V. Dhanabal, R. Karvembu, V. Chinnusamy, and K. Natarajan. *Appl. Organomet. Chem.* **21**, 952 (2007); (c) M.S. Shongwe, B.A. Al-Rashdi, H. Adams, M.J. Morris, M. Mikuriya, and G.R. Hearne. *Inorg. Chem.* **46**, 9558 (2007); (d) H. Zhou, Z.-H. Peng, Z.-Q. Pan, Y. Song, Q.-M. Huang and X.-L. Hu. *Polyhedron*, **26**, 3233 (2007).
- (a) C.W. Leung and M.J. MacLachlan. *J. Inorg. Organomet. Polym. Mater.* **17**, 57 (2007); (b) D. Vitalini, P. Mineo, S. Di Bella, I. Fragala, P. Maravigna, and E. Scamporrino. *Macromolecules*, **29**, 4478 (1996).
- (a) A. Pietrangelo, B.C. Sih, B.N. Boden, Z. Wang, Q. Li, K.C. Chou, M.J. MacLachlan, and M.O. Wolf. *Adv. Mater.* **20**, 2280 (2008); (b) R.P. Kingsborough and T.M. Swager. *Adv. Mater.* **10**, 1100 (1998); (c) R.P. Kingsborough and T.M. Swager. *J. Am. Chem. Soc.* **121**, 8825 (1999); (d) R.P. Kingsborough and T.M. Swager. *Chem. Mater.* **12**, 872 (2000); (e) J.L. Reddinger and J.R. Reynolds. *Synth. Met.* **84**, 225 (1997); (f) J.L. Reddinger and J.R. Reynolds. *Macromolecules*, **30**, 673 (1997); (g) J.L. Reddinger and J.R. Reynolds. *Chem. Mater.* **10**, 3 (1998); (h) T. Shioya and T.M. Swager. *Chem. Commun. (Cambridge)*, 1364 (2002).
- J. Sicé. *J. Am. Chem. Soc.* **75**, 3697 (1953).
- (a) G. Henrio, G. Ple, and J. Morel. *Comptes Rendus des Séances de l'Académie des Sciences*, **278**, 125 (1974); (b) P.

- Netchitailo, B. Decroix, J. Morel, and P. Pastour. *J. Heterocyclic Chem.* **15**, 337 (1978).
9. This compound has been previously prepared (see ref. 8*b*), but via deprotection with pyridine hydrochloride. We found that BBr_3 was more effective.
 10. J. Gradinura, A. Forni, V. Druta, F. Tessore, S. Zecchin, S. Quici, and N. Garbalau. *Inorg. Chem.* **46**, 884 (2007).
 11. G. Zotti, R.A. Marin, and M.C. Gallazzi. *Chem. Mater.* **9**, 2945 (1997).
 12. C. Ma, A. Lo, A. Abdolmaleki, and M.J. MacLachlan. *Org. Lett.* **6**, 3841 (2004).
 13. D.-H. Kim, M.J. Choi, and S.-K. Chang. *Bull. Korean Chem. Soc.* **21**, 145 (2000).