Supporting Information

Nonlinear Optical Properties of Schiff Base-Containing
Conductive Polymer Films Electrodeposited in Microgravity

By Agostino Pietrangelo, Bryan C. Sih, Britta N. Boden, Zhenwei Wang, Qifeng Li, Keng
C. Chou*, Mark J. MacLachlan*, Michael O. Wolf*

[*] B. N. Boden, Prof. K. C. Chou, Dr. Q. Li, Prof. M. J. MacLachlan, A. Pietrangelo,
B. C. Sih, Dr. Z. Wang, Prof. M. O. Wolf
Department of Chemistry
University of British Columbia
2036 Main Mall, Vancouver, British Columbia
Canada V6T 1Z1
E-mail: mwolf@chem.ubc.ca, mmaclach@chem.ubc.ca, kcchou@chem.ubc.ca
Experimental

**General.** Trans-PdCl$_2$(PPh$_3$)$_2$ was obtained from Strem Chemicals; all other reagents were obtained from Aldrich and used without further purification. 5-Thienylsalicylaldehyde$^1$ (1) and alkoxy-substituted diamines$^{2,3}$ 3 and 4 were prepared according to literature procedures for related compounds. All reactions were performed using standard Schlenk techniques with dry solvents under a nitrogen atmosphere. Solution electronic absorption spectra were obtained on a Varian Cary 5000 UV-vis/NIR spectrometer in CH$_2$Cl$_2$ and solid state absorption spectra were acquired on films deposited on ITO. Transmission IR spectra were obtained on a Bomem MB-series spectrometer using KBr pellets. $^1$H and $^{13}$C NMR spectra were acquired on a Bruker AV-300 or AV-400 spectrometer, and spectra were referenced to residual protonated solvent. High resolution electrospray (ESI) or electron impact (EI) ionization mass spectra and elemental analyses were performed at the UBC Microanalytical Services Laboratory. Scanning electron microscopy (SEM) images were taken using a Hitachi S4700 electron microscope operating at 5 kV. Films were imaged directly on Au/Si electrodes used for electrodeposition.

**Electrochemistry.** Cyclic voltammetry experiments were conducted using a Pine AFCBP1 bipotentiostat. The working electrode was either 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 the saturated calomel electrode (SCE). [(n-Bu)$_4$N]PF$_6$ was used as a supporting electrolyte and was purified by triple recrystallization from ethanol and dried at 90 ºC
under vacuum for 3 days. Dichloromethane used for CV was purified by passing the solvent through an activated alumina tower.

**Electropolymerization in Microgravity.** Electrochemical polymerization was carried out in a home-built instrument that features four sealed electrochemical cells cut into a Delrin® block, each equipped with three individually-addressable electrodes for electropolymerization experiments. LABView software on a laptop computer enables time- and voltage-controlled electrochemical processes with in situ current measurements. A silver wire (reference electrode), platinum wire (counter electrode) and Au on glass (working electrode) were used. The deposition solution consisted of 1 mM monomer dissolved in dry dichloromethane containing 0.1 M [(n-Bu)_4N]PF_6. Deposition was carried out by electrolysis at 1.5 V vs. Ag quasi reference electrode for 10 s. For polymers grown in microgravity, electropolymerization was initiated manually onboard the Canadian Space Agency’s (CSA) Falcon 20, a commercial jet with modified hydraulic and fuel systems, for the period of 15 – 20 s when microgravity conditions were present during the parabolic flight path. For comparison, polymers were also electropolymerized at 1 g using the same conditions immediately after landing. All electropolymerized polymers were undoped by applying a potential of 0 V to the working electrode for 60 s.

*N, N'-Phenylenebis(5-(2-thienyl))salicylidenimine (5).* Under a nitrogen atmosphere, 5-thienylsalicylaldehyde 1 (0.475 g, 2.33 mmol) and 1,2-phenylenediamine 2 (0.306 g, 0.992 mmol) were dissolved in anhydrous THF (40 mL) and heated to reflux overnight. The orange solution was then cooled to room temperature and concentrated *in vacuo.*
Addition of methanol to the solution precipitated an orange solid, which was collected on a Büchner funnel and washed with methanol. Compounds 6 and 7 were synthesized in a similar fashion using the corresponding 4,5-disubstituted-1,2-phenylenediamine derivatives.

\[ R = H (5) \]. Yield: 66%. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta \) 13.09 (2H, s, \( OH \)), 8.68 (2H, s, \( CH=\text{N} \)), 7.61 (4H, s, aromatic \( CH \)), 7.36 (2H, dd, \( J = 3.4, 5.9 \) Hz, aromatic \( CH \)), 7.26 (2H, dd, \( J = 3.5, 5.8 \) Hz, aromatic \( CH \)), 7.20 (2H, d, \( J = 8.3 \) Hz, aromatic \( CH \)), 7.19 (2H, d, \( J = 6.8 \) Hz, aromatic \( CH \)), 7.08-7.03 (4H, m, aromatic \( CH \)). \(^{13}\)C NMR (CDCl\(_3\), 75.5 MHz): \( \delta \) 163.4, 161.0, 143.6, 142.4, 131.2, 129.5, 128.0, 128.0, 125.9, 124.0, 122.3, 119.6, 119.2, 118.2. HRMS (ESI): Found: M+H, 481.1046. \( C_{28}H_{21}N_2O_2S_2 \) requires 481.1044. IR (KBr): \( \nu = 3443, 3022, 2923, 2855, 1617, 1481, 1285, 1166, 818, 753, 698 \) cm\(^{-1}\). Anal. Calcd for \( C_{28}H_{20}N_2O_2S_2 \): C, 69.97; N, 5.83; H, 4.19. Found: C, 69.75; N, 5.72; H, 4.34. mp = 206-209°C.

\[ R = OC_6H_13 (6) \]. Yield: 91%. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \( \delta \) 13.24 (2H, s, \( OH \)), 8.63 (2H, s, \( CH=\text{N} \)), 7.60-7.56 (4H, m, aromatic \( CH \)), 7.22-7.18 (4H, m, aromatic \( CH \)), 7.07-7.02 (4H, m, aromatic \( CH \)), 6.82 (2H, s, aromatic \( CH \)), 4.07 (4H, t, \( J = 6.6 \) Hz, \( OCH_2 \)), 1.86-0.88 (22H, m, \( OCH_3C_5H_{11} \)). \(^{13}\)C NMR (CDCl\(_3\), 100.7 MHz): \( \delta \) 161.4, 160.8, 149.3, 143.7, 135.2, 130.8, 129.3, 128.0, 125.8, 123.9, 122.2, 119.3, 118.1, 104.7, 69.8, 31.6, 29.2, 25.7, 22.6. HRMS (ESI): Found: M+H, 681.2823. \( C_{40}H_{48}N_2O_4S_2 \) requires 681.2821. IR (KBr): \( \nu = 3443, 2931, 2856, 1613, 1506, 1482, 1284, 1260, 1177, 816, 693 \) cm\(^{-1}\). Anal. Calcd for \( C_{40}H_{44}N_2O_4S_2 \): C, 70.56; N, 4.11; H, 6.51. Found: C, 70.45; N, 4.16; H, 6.60. mp = 182-189°C.
\( R = OC_{12}H_{25} (7) \). Yield: 64\%. \( ^1H \) NMR (CDCl\(_3\), 300 MHz): \( \delta \) 13.24 (2H, s, OH), 8.64 (2H, s, CH=N), 7.59 (4H, m, aromatic CH), 7.07 (4H, m, aromatic CH), 7.18 (4H, m, aromatic CH), 6.83 (2H, s, aromatic CH) 4.07 (4H, t, \( J = 6.5 \text{ Hz, OCH}_2 \)), 1.86 (4H, m, OCH\(_2\)CH\(_2\)), 1.49-1.47, (36H, m, CH\(_2\)), 0.88 (6H, t, \( J = 6.8 \text{ Hz, CH}_2\text{CH}_3 \)). \( ^{13}C \) NMR (CD\(_2\)Cl\(_2\), 100.7 MHz): \( \delta \) 162.15, 161.25, 149.98, 144.18, 135.86, 131.21, 129.86, 128.65, 126.40, 124.54, 122.81, 120.11, 118.31, 105.18, 70.31, 32.53, 30.31, 30.25, 30.02, 29.97, 29.92, 26.65, 23.29, 14.46. HRMS (ESI): Found: M+H, 849.4698. \( C_{52}H_{69}N_2O_4S_2 \) requires 849.4699. IR (KBr): \( \nu = 2920, 2843, 1616, 1507, 1475, 1274, 1169, 807, 678 \text{ cm}^{-1} \). Anal. Calcd for \( C_{52}H_{68}N_2O_4S_2 \): C, 73.54; H, 8.07; N, 3.30; found: C, 73.50; H, 8.10; N, 3.34. mp = 156 °C.

**Vanadyl complex (5a).** Compound 5 (0.283 g, 589 mmol) and vanadyl acetylacetonate (0.307 g, 1.135 mmol) were dissolved in 20 mL of anhydrous THF. The resulting brown solution was heated to reflux overnight. After cooling, the volume of the solvent was reduced, and addition of methanol precipitated a brown solid. The product was collected on a Büchner funnel and washed with methanol and hexanes. Compounds 6a and 7a were prepared similarly using the substituted derivatives 6 and 7, respectively.

\( R=H (5a) \). Yield: 85\%. MS (ESI): (M + Na\(^+\)) 568.1. IR (KBr): \( \nu = 3455, 3067, 2923, 1610, 1576, 1521, 1465, 1377, 1311, 1178, 982, 815 \text{ cm}^{-1} \). Anal. Calcd for \( C_{28}H_{18}N_2O_3S_2V \): C, 61.65; N, 5.13; H, 3.33. Found: C, 61.57; N, 5.04; H, 3.73. mp = 279-286 °C (dec).

\( R=O\text{C}_{13}H_{13} (6a) \). Yield: 61\%. MS (ESI): (M + Na\(^+\)) 768.2. IR(KBr): \( \nu = 3448, 3068, 3017, 2924, 2858, 1612, 1582, 1520, 1506, 1464, 1371, 1310, 1271, 1176, 1116, 980, 822 \text{ cm}^{-1} \).
cm$^{-1}$. Anal. Calcd for C$_{40}$H$_{42}$N$_2$O$_5$S$_2$V: C, 64.41; N, 3.76; H, 5.68. Found: C, 64.49; N, 3.93; H, 5.80. mp >300˚C.

$R = OC_{12}H_{25}$ (7a). Yield: 85%. HRMS (EI): Found: M$^+$, 913.3859. C$_{52}$H$_{66}$N$_2$O$_5$S$_2$V requires 913.3853. IR (KBr): $\nu = 2924, 2847, 1607, 1519, 1462, 1374, 1265, 1169, 1108, 975, 818, 686, 609, 512$ cm$^{-1}$. Anal. Calcd for C$_{52}$H$_{66}$N$_2$O$_5$S$_2$V + 2 H$_2$O: C, 65.73; N, 2.95; H, 7.43. Found: C, 66.01; N, 2.94; H, 7.70. mp = 223 ˚C.

Nickel complex (5b). Compound 5b was prepared similarly to 5a using nickel(II) acetate tetrahydrate instead of vanadyl acetylacetonate. Compounds 6b and 7b were also prepared in the same manner using the substituted derivatives 6 and 7, respectively.

$R=H$ (5b). Yield: 96%. $^1$H NMR (DMSO-$d_6$, 300 MHz) δ 9.22 (2H, s, C$\equiv$H$_N$), 8.17 (2H, dd, $J = 3.1, 5.7$ Hz, aromatic C$\equiv$H), 7.91 (2H, d, $J = 2.0$ Hz, aromatic C$\equiv$H), 7.69 (2H, dd, $J = 2.1, 9.0$ Hz, aromatic C$\equiv$H), 7.43 (2H, d, $J = 5.2$ Hz, aromatic C$\equiv$H), 7.37 (2H, dd, $J = 2.8, 5.9$ Hz, aromatic C$\equiv$H), 7.33 (2H, d, $J = 3.6$ Hz, aromatic C$\equiv$H), 7.09 (2H, dd, $J = 3.7, 4.8$ Hz, aromatic C$\equiv$H), 6.96 (2H, d, $J = 9.0$ Hz, aromatic C$\equiv$H). HRMS (ESI): Found: M + H, 537.0245. C$_{28}$H$_{19}$N$_2$O$_2$S$_2$Ni requires 537.0241. IR (KBr): $\nu = 3259, 3064, 2956, 1612, 1579, 1520, 1469, 1381, 1332, 1180, 1062, 926, 819, 745$ cm$^{-1}$. Anal. Calcd for C$_{28}$H$_{18}$N$_2$O$_2$S$_2$Ni: C, 62.59; H, 3.38; N, 5.21. Found: C, 62.20; H, 3.52; N, 5.26. mp >300˚C.

$R=OC_6H_{13}$ (6b). Yield: 86%. $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.91 (2H, s, CH=N), 7.52 (2H, d, $J = 2.3$ Hz, aromatic C$\equiv$H), 7.47 (2H, dd, $J = 2.4, 9.0$ Hz, aromatic C$\equiv$H), 7.14-7.04 (6H, m, aromatic C$\equiv$H), 7.02 (2H, s, aromatic C$\equiv$H), 6.99 (2H, dd, $J = 3.7, 4.9$ Hz, aromatic C$\equiv$H), 4.06 (2H, t, $J = 6.6$ Hz, OCH$_2$), 1.86-0.92 (22H, m, OCH$_2$C$_5$H$_{11}$). HRMS (ESI): Found: M + H, 737.2018. C$_{40}$H$_{43}$N$_2$O$_4$S$_2$Ni requires 737.2020. IR (KBr): $\nu = 3439,
2927, 2856, 1615, 1465, 1362, 1281, 1178, 816, 695 cm$^{-1}$. Anal. Calcd for C$_{40}$H$_{42}$O$_{4}$N$_{2}$S$_{2}$Ni: C, 65.13; H, 5.74; N, 3.80. Found: C, 64.86; H, 5.88; N, 4.30. mp >300˚C.

$R = OC_{12}H_{25}$ (7b). Yield: 75%. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.95 (2H, s, C=H=N), 7.52 (4H, m, aromatic CH), 7.05 (2H, m, aromatic CH), 6.99 (2H, aromatic CH) 4.06 (4H, m, OCH$_2$CH$_2$), 1.86 (4H, m, OCH$_2$CH$_2$), 1.50-1.25, (36H, m, CH$_2$CH$_3$). HRMS (EI): Found: M$^+$, 904.3826. C$_{52}$H$_{66}$O$_2$N$_2$S$_2$Ni requires 904.3818. IR (KBr): $\nu$ = 2923, 2847, 1615, 1515, 1463, 1354, 1277, 1169, 815, 686 cm$^{-1}$. Anal. Calcd for C$_{52}$H$_{66}$O$_2$N$_2$S$_2$Ni + CH$_3$OH: C, 67.87; H, 7.52; N, 2.99. Found: C, 67.69; H, 7.44; N, 3.06. mp = 225˚C.

Copper complex (5e). Compound 5e was prepared similarly to 5a using copper(II) acetylacetonate instead of vanadyl acetylacetonate. Compounds 6c and 7c were also prepared in the same manner using the substituted derivatives 6 and 7, respectively.

$R=H$ (5c). Yield: 47%. HRMS (ESI): Found: M + H, 542.0182. C$_{28}$H$_{19}$N$_2$O$_2$S$_2$Cu requires 542.0184. IR (KBr): $\nu$ = 3432, 2923, 1613, 1515, 1469, 1381, 1174, 1168, 819, 807, 755 cm$^{-1}$. Anal. Calcd for C$_{28}$H$_{19}$N$_2$O$_2$S$_2$Cu + H$_2$O: C, 60.04; H, 3.60; N, 5.00. Found: C, 60.08; H, 3.96; N, 4.84. mp = 261-276˚C.

$R=OC_{6}H_{13}$ (6c). Yield: 55%. HRMS (ESI): Found: M + H, 742.1959. C$_{40}$H$_{43}$N$_2$O$_4$S$_2$Cu requires 742.1960. IR (KBr): $\nu$ = 3426, 3072, 2954, 2851, 1611, 1587, 1513, 1469, 1375, 1276, 1172, 815 cm$^{-1}$. Anal. Calcd for C$_{40}$H$_{43}$N$_2$O$_4$S$_2$Cu: C, 64.71; H, 5.70; N, 3.77. Found: C, 64.32; H, 5.82; N, 3.79. mp > 300˚C.

$R=OC_{12}H_{25}$ (7c). Yield: 64%. HRMS (EI): Found: M$^+$, 911.3756. C$_{52}$H$_{66}$N$_2$O$_2$S$_2$Cu requires 911.3742. Found 911.3756. IR (KBr): $\nu$ = 2919, 2855, 1607, 1515, 1463, 1374,
1277, 1173, 1116, 819, 694 cm\(^{-1}\). Anal. Calcd for C\(_{52}\)H\(_{66}\)N\(_2\)O\(_4\)S\(_2\)Cu: C, 68.57; H, 7.30; N, 3.08. Found: C, 68.20; H, 7.38; N, 3.10. mp = 178°C.

*X-ray crystallographic analysis.* All X-ray data for structures 7b and 7c were collected on a Bruker X8 APEX diffractometer using Mo-K\(\alpha\) radiation. Data were collected at -100.0 ± 0.1°C in four scan sets using 0.50° oscillations and exposure times of 30 seconds. All data were collected and integrated using the Bruker SAINT\(^{[4]}\) software package and corrected for absorption using SADABS.\(^{[5]}\) The structures were solved by direct methods.\(^{[6]}\) All refinements were performed using the SHELXTL.\(^{[7]}\) crystallographic software package of Bruker-AXS. Complex 7b crystallizes in space group P-1 with two molecules of ethanol in the asymmetric unit. Both thiophene rings are disordered by rotation about the C4-C5 and C15-C19 bonds, respectively. The disorder was modeled with constraints on C-S and C-C bond distances. All hydrogen atoms involved in hydrogen-bonding were located in difference maps and refined isotropically, while all other hydrogen atoms were included in calculated positions but not refined. Complex 7c crystallizes in space group P2\(_1\)/c with one molecule of solvent methanol in the asymmetric unit. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms involved in hydrogen-bonding were located in difference maps and refined isotropically, while all other hydrogen atoms were included in calculated positions but not refined.

*Nonlinear optical measurements.* An amplified Ti:sapphire laser with an output at 800 nm, a pulse duration of 130 fs, and a repetition rate of 1 kHz was used for third harmonic generation (THG) in reflection geometry. The incident beam was p-polarized with an incident angle of 45°. A series of mirrors, bandpass filters, and a monochromator
were used to separate the fundamental 800 nm beam and the THG. The THG intensity was detected by a photomultiplier tube (PMT) and a gated integrator. The energy of the incident laser beam is typically below 3 \( \mu J \) per pulse. At this energy level, the THG contributions from air and other optics were found to be negligible.

To compare the THG from the polymer films to the reference silica window, the intensity of THG can be written as

\[
I(3\omega) \propto \left| \chi_{\text{eff}}^{(3)} \right|^2 \times I_m^3(\omega) \times d^2 \times l_c^2
\]

where \( \chi_{\text{eff}}^{(3)} \) is the effective third-order nonlinear susceptibility, \( I_m(\omega) \) is the incident beam intensity, \( d \) is the thickness of the film, and \( l_c \) is the coherence length. Using the third-order nonlinear susceptibility of silica, \( \chi_r^{(3)} \), as the calibration reference, the third-order nonlinear susceptibility of the polymers, \( \chi_s^{(3)} \), can be derived as

\[
\left| \chi_s^{(3)} \right| = \left| \chi_r^{(3)} \right| \times \frac{\sqrt{I_s}}{\sqrt{I_r}} \times \frac{\sqrt{F_r}}{\sqrt{F_s}} \times \frac{d_c}{d_s} \times \frac{l_c'}{l_s'}
\]

(1)

where \( d_s \) is the sample thickness and \( F_r^R \) and \( F_s^R \) are the Fresnel factors for silica and the samples, respectively. The dielectric constants used to determine the Fresnel factors of polymers were obtained using ellipsometry. With \( d_r = \lambda / 2\pi = 127.3 \text{ nm} \), \( l_c' = 16.4 \text{nm} \), \( l_c'' = 12.6 \text{nm} \), and \( F_r^R = 1.8110 \) and \( F_s^R = 0.0356 \), the third-order nonlinear susceptibilities of the polymers, \( \chi_s^{(3)} \), were determined using equation (1).

References