

SUPPORTING INFORMATION ACCOMPANYING:

**Direct Insights into Metal-Induced Conductivity Enhancement in
Conducting Metallopolymers**

Minh T. Nguyen and Bradley J. Holliday*

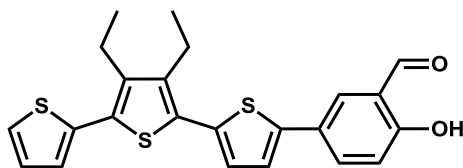
*Department of Chemistry, The University of Texas at Austin, 105 E. 24th St., Stop A5300,
Austin, TX 78712-0165*

General Methods	S2
Synthesis of ligand precursors, ligands, and vanadyl complexes	S2
Electrochemistry	S6
UV-Vis-NIR spectroelectrochemistry	S7
Conductivity measurements	S7
Computational methods	S8
Crystal structure determination	S8
Table S1. Crystal data and structure refinement of 3	S9
Figure S1. EPR spectrum of 6	S10
Figure S2. Electropolymerization of mono-thiophene substituent ligand, L¹	S11
Figure S3. Scan rate dependence studies of poly- 4 and poly- 6	S12
Figure S4. XPS data of poly- 6	S13
References	S14

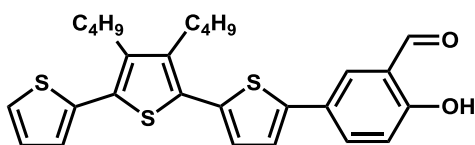
General Methods

Air- and moisture-sensitive reactions were carried out in oven-dried glassware using standard Schlenk techniques under an inert nitrogen atmosphere. All chemicals were purchased from commercial sources and used as received. Dry solvents were dried using an Innovative Technology, Pure Solv solvent purifier with a double purifying column. ^1H NMR (400 MHz) and ^{13}C { ^1H } NMR (100 MHz) spectra were obtained on a Varian (400 MHz) spectrometer and were referenced to residual solvent peaks. All peak positions are given in ppm and coupling constants are reported in Hz. Low-resolution and high-resolution mass spectrometry was carried out by a Thermo Finnigan TSQ 700 and Waters Autospec Ultima, respectively. Melting points were recorded with an OptiMelt Automated Melting Point System with digital image processing technology from Stanford Research System (SRS, Sunnyvale, CA). Melting points were obtained in open glass capillaries and are uncorrected. Elemental analysis was performed by Midwest Microlab, Indianapolis, IN (www.midwestlab.com). Infrared spectra were recorded using a Nicolet IR 200 FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) was carried out on a PHI 5700 XPS system equipped with dual Mg X-ray source and monochromatic Al X-ray source complete with depth profile and angle-resolved capabilities. Electron paramagnetic resonance (EPR) was recorded on a Bruker EMX-Plus X-band spectrometer at 293 K, 6.33 mW microwave power, and 2 G modulation amplitude.

Synthesis of ligands and vanadyl complexes

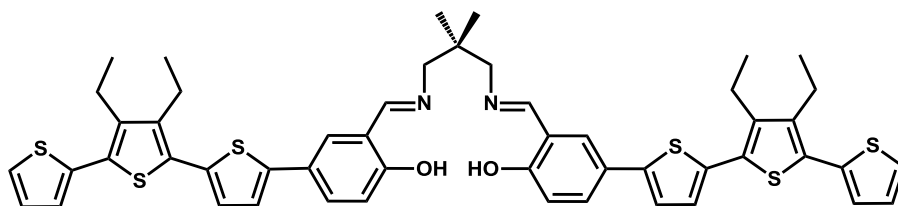


5-(3',4'-diethyl-[2,2':5',2''-terthiophen]-5-yl)-2-hydroxybenzaldehyde (1) To a mixture of 5-bromosalicylaldehyde (1.00 g, 5 mmol), and Pd(PPh₃)₂Cl₂ (0.3 g, 0.88 mmol) in 60 mL of dry toluene was added 2-(tributylstannyl)-3',4'-diethyl-2,2':5',2''-terthiophene¹ (2.97 g, 5 mmol). The reaction mixture was heated to 100 °C for 48 hours under nitrogen. The reaction was cooled and dried *in vacuo*. The mixture was dissolved in CH₂Cl₂, and then filtered through a silica gel plug. The filtrate was washed with dilute NH₄Cl_(aq) (3 times, 80 mL), then dried over MgSO₄. Solvent was removed and the product was purified by column chromatography (silica gel, CH₂Cl₂ : hexanes = 50 : 50) to yield a light orange solid (1.23 g, 58%). FTIR: 3250-2300 (w, O-H), 1647 (s, C=O), 1460 (s, aliphatic C-H bend), 1284 (s, C-O), 688 (s, C-H aromatic) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 11.02 (s, 1H), 9.90 (s, 1H), 7.72 (dd, 1H, *J* = 2.3, 8.4), 7.70 (d, 1H, *J* = 2.3), 7.30 (dd, 1H, *J* = 1.2, 5.1), 7.15 (d, 1H, *J* = 3.9), 7.14 (dd, 1H, *J* = 1.2, 3.6), 7.07 (d, 1H, *J* = 3.9), 7.06 (dd, 1H, *J* = 3.6, 5.1), 7.00 (d, 1H, *J* = 8.4), 2.79 (m, 4H), 1.23-1.30 (m, 6H); ¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) = 196.4, 161.0, 141.9, 141.3, 141.2, 135.9, 135.4, 134.3, 130.3, 130.0, 129.6, 127.4, 126.6, 126.5, 125.9, 125.4, 123.1, 120.6, 118.4, 21.2, 21.0, 15.4, 15.3. HRMS (ESI) *m/z* calculated for C₂₃H₂₀O₂S₃ *m/z* 425.0625 ([M+H]⁺), found 425.0629 ([M+H]⁺).



5-(3',4'-dibutyl-[2,2':5',2''-terthiophen]-5-yl)-2-hydroxybenzaldehyde (2) This compound was prepared in a similar procedure for the diethyl derivative above using 2-(tributylstannyl)-3',4'-dibutyl-2,2':5',2''-terthiophene.¹ Orange solid (1.49 g, 62%). FTIR: 3250-2300 (w, O-H), 1648 (s, C=O), 1460 (s, aliphatic C-H bend), 1283 (s, C-O), 688 (s, C-H aromatic) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 11.02 (s, 1H), 9.90 (s, 1H), 7.72 (dd, 1H, *J* = 2.3, 8.4), 7.70

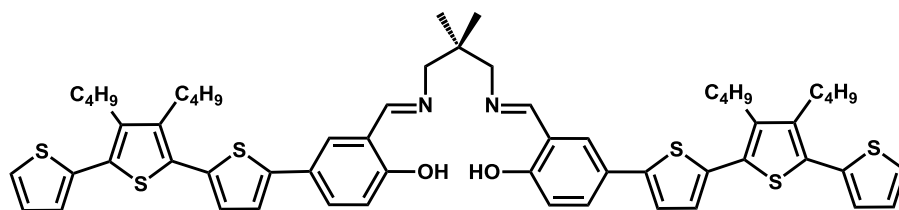
(d, 1H, $J = 2.3$), 7.30 (dd, 1H, $J = 1.2, 5.1$), 7.15 (d, 1H, $J = 3.9$), 7.14 (dd, 1H, $J = 1.2, 3.6$), 7.07 (d, 1H, $J = 3.9$), 7.06 (dd, 1H, $J = 3.6, 5.1$), 7.00 (d, 1H, $J = 8.4$), 2.73 (m, 4H), 1.31-1.66 (m, 8H), 0.96 (m, 6H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3): δ (ppm) = 196.3, 160.8, 141.7, 140.1, 140.0, 139.5, 136.0, 135.5, 134.1, 130.1, 129.9, 129.5, 127.3, 126.5, 125.8, 125.3, 123.0, 120.5, 118.2, 32.8, 32.7, 27.8, 27.7, 23.0, 22.9, 13.8, 13.7. HRMS (ESI) m/z calculated for $\text{C}_{27}\text{H}_{28}\text{O}_2\text{S}_3$ m/z 481.1211 ($[\text{M}+\text{H}]^+$), found 481.1211 ($[\text{M}+\text{H}]^+$).



***N,N'*-((2,2'-dimethylpropyl)bis(3',4'-diethyl-[2,2':5',2''-terthiophen]-5-yl)salicylideneimine**

(3) To a solution of 5-(3',4'-diethyl-[2,2':5',2''-terthiophen]-5-yl)-2-hydroxybenzaldehyde (0.63 g, 1.48 mmol) in CHCl_3 : EtOH = 1 : 2 (30 mL) was added 1,3-diamino-2,2'-dimethylpropane (0.076 g, 0.74 mmol) in 10 mL EtOH. The reaction mixture was stirred at 60 °C overnight resulting in an orange suspension. The precipitate was collected by vacuum filtration to give the desired product (0.63 g, 91%), m.p. 99 °C. FTIR: 3250-2300 (w, O-H), 1633 (s, C=N), 1461 (s, aliphatic C-H bend), 1281 (s, C-O), 670 (s, C-H aromatic) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ (ppm) = 13.66 (s, 2H), 8.38 (s, 2H), 7.57 (dd, 2H, $J = 2.3, 8.6$), 7.47 (d, 2H, $J = 2.3$), 7.29 (dd, 2H, $J = 1.2, 5.2$), 7.12 (d, 2H, $J = 3.7$), 7.10 (d, 2H, $J = 3.7$), 7.06 (dd, 2H, $J = 3.7, 5.2$), 7.04 (d, 2H, $J = 3.7$), 6.99 (d, 2H, $J = 8.6$), 3.51 (s, 4H), 2.75 (m, 8H), 1.22 (m, 12H), 1.09 (s, 6H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3): δ (ppm) = 165.6, 161.0, 143.1, 141.2, 140.9, 136.0, 134.5, 129.9, 129.8, 129.7, 128.4, 127.4, 126.6, 125.8, 125.3, 125.2, 122.4, 118.7, 117.7, 67.9, 36.3, 24.4, 21.1, 21.0, 15.4, 15.3. UV-Vis (λ_{max} (ϵ), CH_2Cl_2): 364 nm (59,300 $\text{cm}^{-1}\text{M}^{-1}$). HRMS (CI+) m/z calculated for $\text{C}_{51}\text{H}_{50}\text{N}_2\text{O}_2\text{S}_6$ m/z 914.2197 ($[\text{M}]^+$), found 914.2192 ($[\text{M}]^+$). Elemental analysis

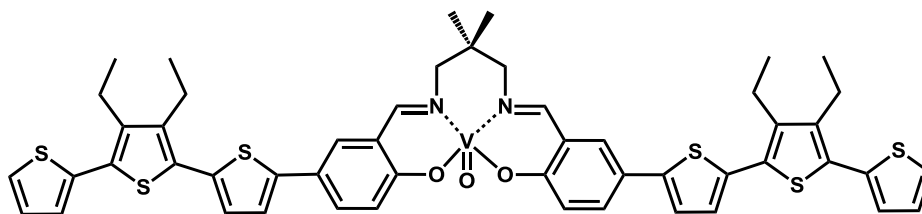
calculated (found): C, 66.92(66.32); H, 5.51(5.39); N 3.06 (2.77).



***N,N'*-((2,2'-dimethylpropyl)bis(3',4'-dibutyl-[2,2':5',2''-terthiophen]-5-yl)salicylideneimine**

(4) This complex was prepared in a manner similar to **3** with a yield of 88% (0.60 g), m.p. 82 °C.

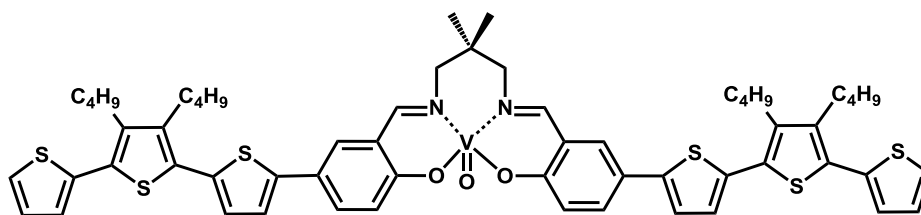
FTIR: 3250-2300 (w, O-H), 1631 (s, C=N), 1462 (s, aliphatic C-H bend), 1284 (s, C-O), 688 (s, C-H aromatic) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ (ppm) = 13.68 (s, 2H), 8.35 (s, 2H), 7.56 (dd, 2H, $J = 2.3, 8.6$), 7.46 (d, 2H, $J = 2.3$), 7.28 (dd, 2H, $J = 1.2, 5.2$), 7.12 (d, 2H, $J = 3.7$), 7.10 (d, 2H, $J = 3.7$), 7.05 (dd, 2H, $J = 3.7, 5.2$), 7.04 (d, 2H, $J = 3.7$), 7.00 (d, 2H, $J = 8.6$), 3.50 (s, 4H), 2.71 (m, 8H), 1.56 (m, 8H), 1.44 (m, 8H), 1.09 (s, 6H), 0.96 (m, 12H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) = 165.5, 161.0, 143.1, 140.2, 139.8, 136.1, 134.6, 133.4, 129.9, 129.8, 129.6, 128.3, 127.3, 126.5, 125.7, 125.2, 122.3, 118.2, 117.63, 68.0, 36.17, 30.84, 27.8, 27.7, 24.3, 24.2, 23.0, 22.9, 13.8, 13.7. UV-Vis (λ_{max} (ϵ), CH_2Cl_2): 362 nm (56,900 $\text{cm}^{-1}\text{M}^{-1}$). HRMS (CI+) m/z calculated for $\text{C}_{59}\text{H}_{66}\text{N}_2\text{O}_2\text{S}_6$ m/z 1026.3444 ($[\text{M}]^+$), found 1026.3449 ($[\text{M}]^+$). Elemental analysis calculated (found) for $\text{C}_{59}\text{H}_{66}\text{N}_2\text{O}_2\text{S}_6 \cdot \text{CH}_2\text{Cl}_2$: C, 64.78(65.63); H, 6.47(6.16); N 2.73 (2.52).



***N,N'*-((2,2'-dimethylpropyl)bis(3',4'-ethyl-[2,2':5',2''-terthiophen]-5-yl)salicylideneiminato**

vanadium(IV)-oxo (5) Ligand **3** (0.25 g, 0.122 mmol) was dissolved in CHCl_3 : EtOH = 1 : 1 (20 mL) and the solution was purged with nitrogen for 5 min. To this solution, a nitrogen-purged

solution of vanadyl acetylacetonate (32.3 mg, 0.122 mmol) in 10 mL of EtOH was added. The reaction mixture was stirred under nitrogen at 60 °C for 1 hr, and then cooled to room temperature. CHCl₃ was removed *in vacuo* resulting in a suspension in EtOH. The light orange solid was isolated by vacuum filtration then further dried under vacuum to give **5** (0.21 g, 89%), m.p. (decomp.) > 228 °C. FTIR: 1622 (s, C=N), 1457 (s, aliphatic C-H bend), 1284 (s, C-O), 863 (s, V=O), 698 (s, C-H aromatic) cm⁻¹. UV-Vis (λ_{max} (ε), CH₂Cl₂): 379 nm (68,200 cm⁻¹M⁻¹). HRMS (CI+) m/z calculated for C₅₁H₄₈N₂O₃S₆V m/z 979.1429 ([M]⁺), found 979.1440 ([M]⁺). Elemental analysis calculated (found): C, 62.49(62.36); H, 4.94(5.00); N 2.86(2.62).



***N,N'*-((2,2'-dimethylpropyl)bis(3',4'-dibutyl-[2,2':5',2''-terthiophen]-5-yl)salicylideneiminato vanadium(IV)-oxo (**6**)** This complex was prepared in a manner similar to **5** using ligand **4** (0.11 g, 83%), m.p. (decomp.) > 226 °C. FTIR: 1618 (s, C=N), 1460 (s, aliphatic C-H bend), 1284 (s, C-O), 875 (s, V=O), 689 (s, C-H aromatic) cm⁻¹. UV-Vis (λ_{max} (ε), CH₂Cl₂): 378 nm (64,700 cm⁻¹M⁻¹). HRMS (CI+) m/z calculated for C₅₉H₆₄N₂O₃S₆V m/z 1091.2671 ([M]⁺), found 1091.2681 ([M]⁺). Elemental analysis calculated (found): C, 64.86(62.56); H, 5.90(5.08); N 2.56(2.70).

Electrochemistry

Electrochemical syntheses and studies were performed in a dry-box under a nitrogen atmosphere using a GPES system from Eco. Chemie B. V. All the electrochemical experiments were carried out in a three-electrode cell with a Ag/AgNO₃ reference electrode (silver wire

dipped in a 0.01 M silver nitrate solution with 0.1 M [(*n*-Bu)₄N][PF₆] in CH₃CN), a Pt button working electrode, and a Pt wire coil counter electrode. Potentials were referenced relative to the 0.01 M Ag/AgNO₃ reference electrode. Ferrocene was used as an external standard to calibrate the reference electrode before and after experiments were performed, and that value was used to correct the measured potentials. The supporting electrolyte was 0.1 M [(*n*-Bu)₄N][PF₆] (TBAPF₆) that was purified by recrystallization three times from hot ethanol before being dried for 3 days at 100-150 °C under active vacuum. Electrosynthesis of the films were performed from 5 × 10⁻⁴ M monomer solutions by continuous cycling between -0.5 V and 1.5 V at 100 mV·s⁻¹. The films obtained were then repeatedly washed with fresh CH₂Cl₂ before continuing on to the next set of experiments.

UV-Vis-NIR spectroelectrochemistry

The spectroelectrochemical measurements were performed using the previously described electrochemical cell arrangement (*vide supra*) with a polymer film electrochemically deposited on ITO-coated glass substrate as the working electrode, a platinum mesh as the counter electrode, and a Ag/AgNO₃ reference electrode. Experiments were carried out in an optical cuvette inside the glovebox. Absorption spectra were recorded on a Varian Cary 6000i UV-Vis-NIR spectrophotometer within the NIR/visible spectra (1600 ≥ λ ≥ 400 nm) under several applied potentials.

Conductivity measurements

The conductivities of polymer films were determined using equation (1).² Interdigitated electrodes were purchased from CH Instrument (CH 012126) with 10 μm interdigit spacing, *D*; *n* = 129 gaps; and 0.2 cm electrode length, *L*. Film thickness, *T*, was obtained on a Dektak 3 surface profilometer. Conductivity profiles were carried at 0.4 V applied offset potential, *V_D*, and

a scan rate 10 mV/s.

$$\sigma = \frac{i_D}{V_D} \times \frac{D}{n \cdot T \cdot L} \quad (1)$$

Computational methods

Optimized structures and frontier molecular orbital diagrams of ligand **3** and vanadyl complex **7** were performed with density functional theory (DFT) using the Gaussian 03 program,³ employing the B3YLP functional in conjunction with the SDD basis set. All geometries were fully optimized using the default optimization criteria of the program. Orbital analyses were completed with GaussView 5.0 program.

Crystal structure determination

The single-crystal diffraction data were collected on a Rigaku SCX-Mini diffractometer with a Mercury CCD using a graphite monochromator with MoK α radiation ($\alpha = 0.71073 \text{ \AA}$). Details of crystal data, data collection, and structure refinement of **3** are listed in Table S1. Data reduction were performed using the Rigaku Americas Corporation's Crystal Clear version 1.40.⁴ Absorption corrections were applied using Multi-scan. The structures were solved by direct methods using SIR97 and refined anisotropically using full-matrix least-squares methods with the SHELX97⁵ program package. The coordinates of the non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in the calculation isotropically but not refined. Residual electron densities in the solvent-accessible void due to disordered solvent molecules were treated with the PLATON/SQUEEZE program. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).⁶

Table S1. Crystal Data and Structure Refinement of **3**.

Empirical formula	C ₅₁ H ₅₀ N ₂ O ₂ S ₆
Formula weight	915.29
Temperature (K)	153(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>C</i> 12/ <i>c</i> 1
<i>a</i> (Å)	37.215
<i>b</i> (Å)	14.101
<i>c</i> (Å)	9.619
α (deg)	90
β (deg)	96.59
γ (deg)	90
Volume (Å ³)	5014.3
<i>Z</i>	4
ρ (mg/cm ³)	1.212
μ (mm ⁻¹)	0.312
F(000)	1928
Crystal size (mm)	0.20 x 0.07 x 0.06
θ (deg)	3.09 to 24.89
Index ranges	-43 ≤ <i>h</i> ≤ 43
	-16 ≤ <i>k</i> ≤ 16
	-11 ≤ <i>l</i> ≤ 11
Reflections collected	21177
Max. and min. transmission	0.9815 and 0.9402
GOF on F^2	1.07
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0725, 0.1735
<i>R</i> 1, <i>wR</i> 2 [all data]	0.1168, 0.1948
Largest diff. peak and hole (e.Å ⁻³)	0.414 and -0.259

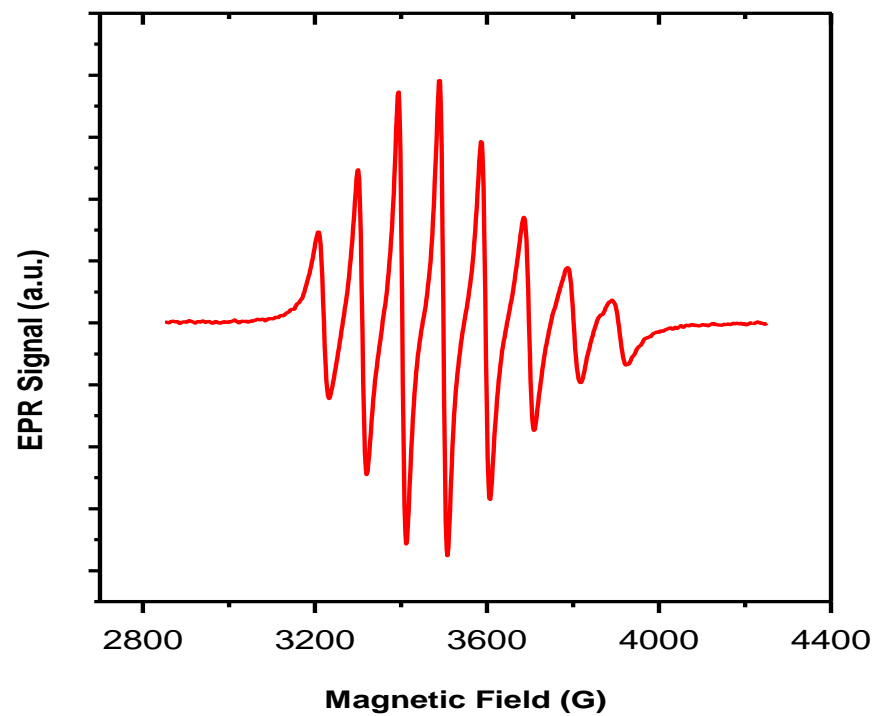
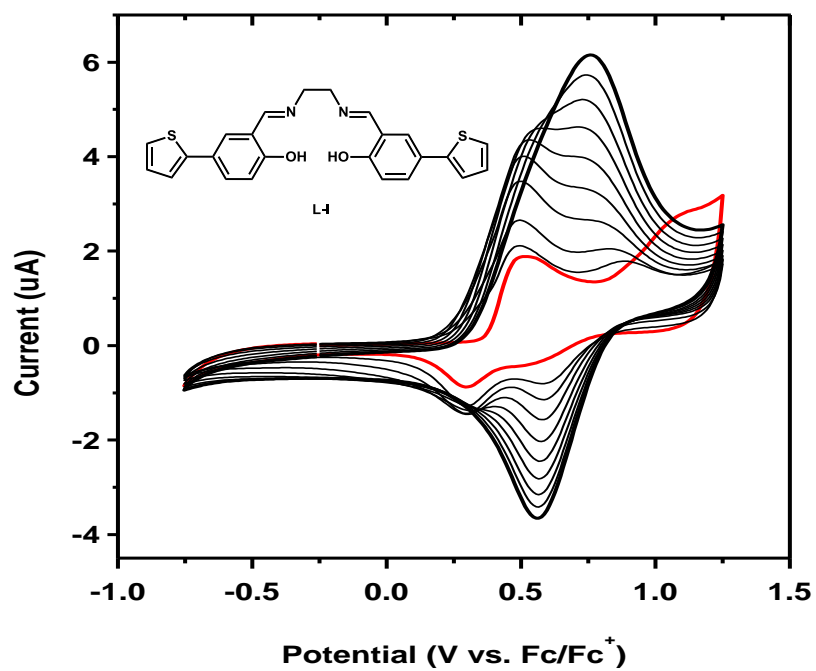


Figure S1. EPR spectra of **6** showing the presence of vanadium center in the complex monomer.

A.



B.

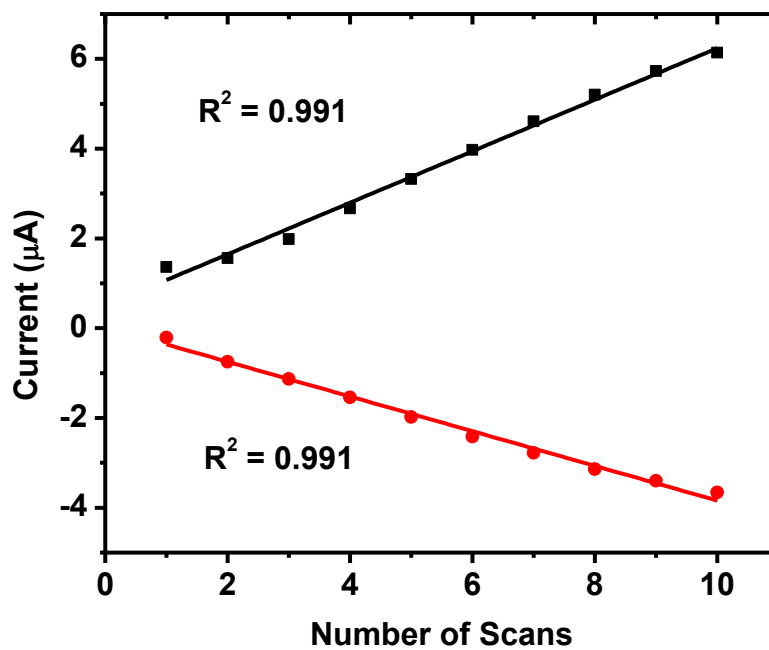
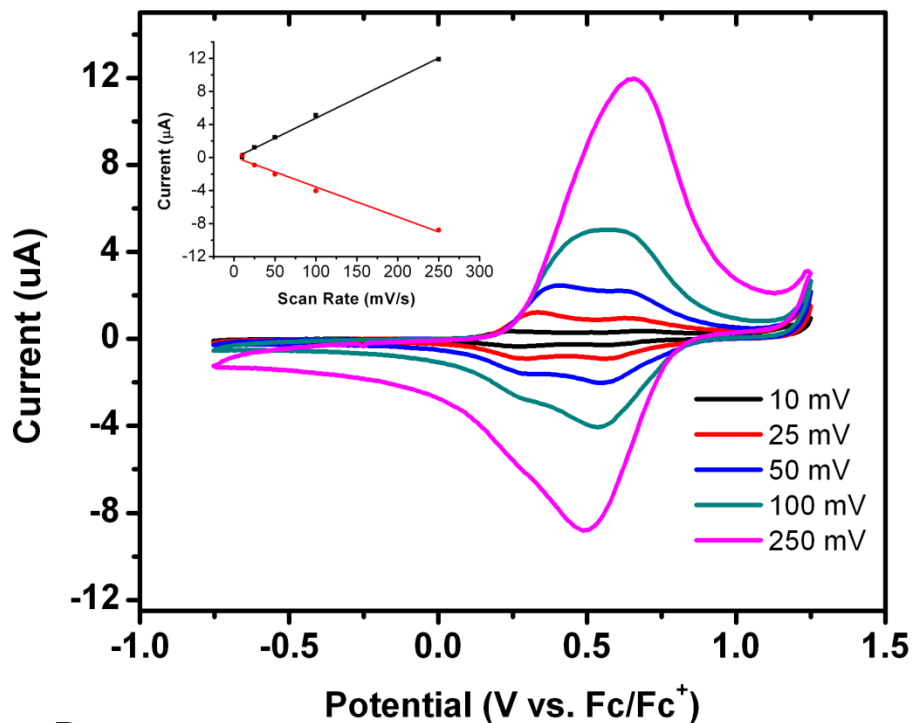


Figure S2. (A) Electropolymerization of mono-thiophene substituted Schiff-base ligand **L1** from a 2×10^{-4} M CH_2Cl_2 solution, 0.1 M TBAPF_6 , Pt button electrode (B) The peak current versus the number of scans.

A.



B.

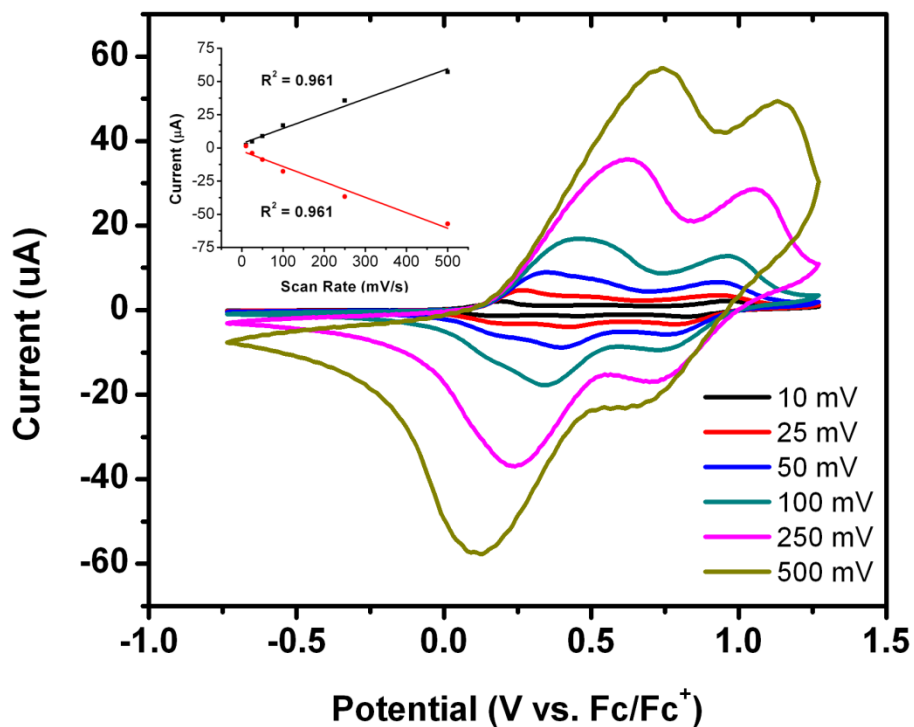
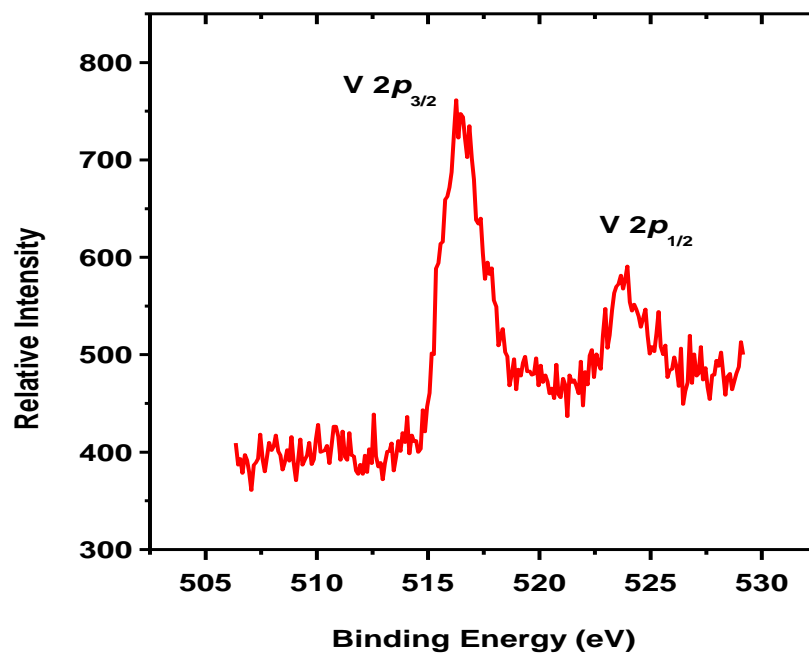


Figure S3. Scan rate dependence of electrode-confined films of **poly-4** (A) and **poly-6** (B) in 0.1 M TBAPF₆/CH₂Cl₂ electrolyte solution. Inset: The peak current versus the scan rates.

A.



B.

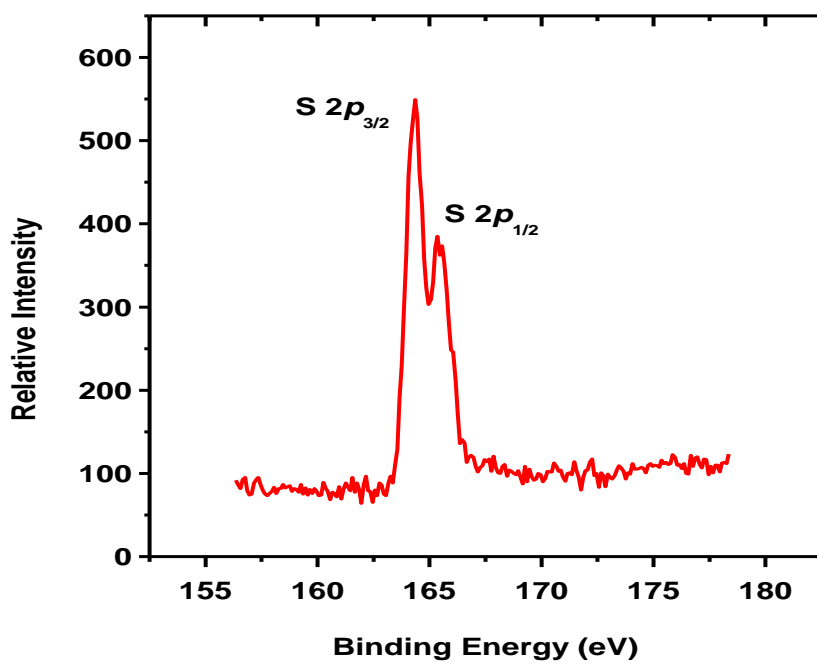


Figure S4. XPS data of poly-6 (A) V 2p (B) S 2p.

References

- 1) S. S. Zhu, T. M. Swager, *J. Am. Chem. Soc.* 1997, **119**, 12568-12577.
- 2) D. L. Simone, T. M. Swager, *J. Am. Chem. Soc.* 2000, **122**, 9300-9301.
- 3) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, K. N. K.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, K.; Toyota, R.; Fukuda, J.; Hasegawa, M.; Ishida, T.; Nakajima, Y.; Honda, O.; Kitao, H.; Nakai, M.; Klene, X.; Li, J. E.; Knox, H. P.; Hratchian, J. B.; Cross, V.; Bakken, C.; Adamo, J.; Jaramillo, R.; Gomperts, R. E.; Stratmann, O.; Yazyev, A. J.; Austin, R.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Revision B.04; Gaussian, Inc.: Wallingford, CT, 2003.
- 4) A. Altomare, Burla, M. M. C. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* 1999, **32**, 115-119.
- 5) G. M. Sheldrick, *SHELXL97: Program for the Refinement of Crystal Structures*, University of Gottingen: Gottingen, Germany, 1994.
- 6) *International Tables for X-ray Crystallography*, A. J. C. Wilson, Ed.; Kluwer Academic Press: Boston, 1992; Vol. C.