SUPPORTING INFORMATION ACCOMPANYING:

Effect of Conjugation Length and Metal-Backbone Interactions on Charge Transport Properties of Conducting Metallopolymers

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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 obtained using an Innovative Technology, Pure Solv solvent purifier with a double purifying column. ¹H NMR (400 MHz) and ¹³C{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 using a Thermo Finngan 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) and the uncorrected values are reported. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN (www.midwestlab.com. Ligands 1-3,¹⁻³ 4, 7, 10, 13,¹ 14,⁴ 18 complexes were prepared using previously reported procedures.¹⁻³ Other commercially available reagents were used without further purification.

Synthesis. 5. This complex was prepared in a manner similar to 4 using ligand 2.¹ 73% orange solid, mp > 250 °C. UV-Vis (λ_{max} (ϵ), CH₂Cl₂): 359 nm (68,900 cm⁻¹M⁻¹). HRMS (CI⁺) m/z calculated for [C₃₅H₂₈N₂O₃S₄V]⁺ ([**5**]⁺): 703.0422, found 703.0410. Elemental analysis calculated (found): C, 59.73(59.47); H, 4.01(4.09); N 3.98(3.90). Crystals suitable for X-ray analysis were grown *via* slow diffusion of acetonitrile to a dimethylformaldehyde solution.

8. This complex was prepared in a manner similar to **5** using $Co(OAc)_2 \cdot 4H_2O$. 73% yellow-brown solid, mp > 250 °C. UV-Vis (λ_{max} (ϵ), CH₂Cl₂): 365 nm (62,500 cm⁻¹M⁻¹). HRMS (CI⁺) m/z calculated for $[C_{35}H_{28}N_2O_2S_4Co]^+$ ([**8**]⁺): 695.0366, found 695.0370. Elemental analysis calculated (found) for (CoL^{II})₂·2H₂O: C, 57.44(57.94); H, 4.41(4.20); N 3.83(3.68).

Crystals suitable for X-ray analysis were grown *via* slow evaporation of a dichloromethane/acetonitrile solution.

11. This complex was prepared in a manner similar to **5** using Ni(OAc)₂·4H₂O. 98% dark green solid, mp > 250 °C. ¹H NMR 8.35 (s, 2H), 7.56 (dd, 2H, J = 2.3, 8.6), 7.46 (d, 2H, J = 2.3), 7.18 (dd, 2H, J = 1.2, 5.1), 7.15 (dd, 2H, J = 1.2, 3.6), 7.04 (dd, 2H, J = 3.5, 5.1), 6.99 (d, 2H, J = 8.6), 3.51 (s, 4H), 1.09 (s, 6H). ¹³C {¹H} NMR: compound is not sufficiently soluble in any common solvent to obtain a spectrum. UV-Vis (λ_{max} (ϵ), CH₂Cl₂): 360 nm (49,000 cm⁻¹M⁻¹). HRMS (CI⁺) m/z calculated for [C₃₅H₂₈N₂O₂S₄Ni]⁺ ([11]⁺): 694.0387, found 694.0385. Elemental analysis calculated (found): C, 60.44(60.34); H, 4.06(4.31); N 4.03(3.90). Crystals suitable for X-ray analysis were grown *via* slow evaporation of a dichloromethane/ethanol solution.

19. This complex was prepared in a manner similar to **18** using $Co(OAc)_2 \cdot 4H_2O.^3$ 73% yellow-brown solid, mp > 250 °C. UV-Vis (λ_{max} (ϵ), CH₂Cl₂): 381 nm (54,700 cm⁻¹M⁻¹). HRMS (CI⁺) m/z calculated for [C₅₉H₆₆N₂O₃S₆Co]⁺ ([**19**]⁺): 1083.2624, found 1083.2615. Elemental analysis calculated (found) for **19**·(CHCl₃)(H₂O)₂: C, 61.49(61.10); H, 5.77(5.49); N 2.41(2.60).

20. This complex was prepared in a manner similar to **18** using Ni(OAc)₂·4H₂O.³ 73% yellow-brown solid, mp > 250 °C. ¹H NMR 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). ¹³C {¹H} NMR: compound is not sufficiently soluble in any common solvent to obtain a spectrum. UV-Vis (λ_{max} (ϵ), CH₂Cl₂): 390 nm (72,400 cm⁻¹M⁻¹). HRMS (CI⁺) m/z calculated for [C₅₉H₆₆N₂O₃S₆Ni]⁺ ([**20**]⁺): 1082.2646, found 1082.2653. Elemental analysis calculated (found) for **20**·H₂O: C, 64.29(62.23); H, 6.04(5.86); N 2.54(2.66).

Crystals suitable for X-ray analysis were grown *via* slow diffusion of ethanol into a dichloromethane solution.

21. This complex was prepared in a manner similar to **18** using Cu(OAc)₂. 98% bright green solid, mp > 250 °C. UV-Vis (λ_{max} (ϵ), CH₂Cl₂): 385 nm (76,500 cm⁻¹M⁻¹). HRMS (CI⁺) m/z calculated for [C₅₉H₆₆N₂O₃S₆Cu]⁺ ([**21**]⁺): 1087.2588, found 1087.2591. Elemental analysis calculated (found) for **21**·H₂O: C, 64.01(64.04); H, 6.01(5.84); N 2.53(2.58). Crystals suitable for X-ray analysis were grown *via* slow diffusion of ethanol into a dichloromethane solution.

X-ray structure Determination. Single-crystal X-ray diffraction data were collected on a Rigaku AFC12 diffractometer, a Saturn 724+ CCD or a Rigaku SCX-Mini diffractometer with a Mercury CCD using a graphite monochromator with MoK α radiation ($\alpha = 0.71070$ Å). Absorption corrections were applied using Multi-scan. Data reduction were performed using the Rigaku Americas Corporation's Crystal Clear version 1.40.5 The structures were solved by direct methods using SIR97⁶ and refined anisotropically using full-matrix least-squares methods with the SHELX 97⁷ program package. The coordinates of the non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in the calculation isotropically but not refined. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).8 CCDC deposition numbers 1544968, 1545045, 1544969, 1544970, 1544971, and 1544972 for 1, 5, 8, 11, 20, and 21, respectively. There are a high free weight R-factor and a low precision on C-C bonds in the X-ray structure of 21 resulting in one B alert in its CheckCif, which is mainly due to disorder of the n-butyl groups and solvent molecules (CH₂Cl₂) in the lattice of **21**. Details of structure refinement can be found in the Cif file of 21 in the ESI.

Electrochemistry. Electrochemical studies were performed in a dry-box under a nitrogen atmosphere utilizing a Metrohm Eco Chemie Autolab PGSTAT30 potentiostat/galvanostat with a FRA2-module for electrochemical impedance studies and a bipotentiostat module. The software interface utilized to obtain and process the data was the General Purpose Electrochemical Software (GPES) supplied by the potentiostat manufacturer. All the electrochemical experiments were carried out in a three-electrode cell with Ag/AgNO₃ reference electrode (silver wire dipped in a 0.01 M silver nitrate solution with 0.1 M [(n-Bu)₄N][PF₆] (TBAPF₆) in CH₃CN), a Pt working electrode, and Pt wire coil counter electrode. Potentials were relative to this 0.01 M Ag/AgNO₃ reference electrode. Ferrocene was used as an external reference to calibrate the reference electrode before and after experiments were performed and that value was used to correct the measured potentials. All electrochemistry and electropolymerizations were performed in dry CH₂Cl₂ or dry acetonitrile (CH₃CN) using 0.1 M TBAPF₆ as the supporting electrolyte. The TBAPF₆ was purified by recrystallization three times from hot ethanol before being dried for 3 days at 100-150 °C under dynamic vacuum prior to use. Electrosyntheses of polymer films were performed from 0.5 and 1.0 mM solutions of the ligand and metal complexes, respectively, by continuous cycling between -0.75 V and 1.25 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.

Spectroelectrochemistry. The *in situ* vis-NIR absorption-based spectroelectrochemical measurements were performed using the cell arrangement described immediately above with a polymer film electrochemically deposited on indium-tin-oxide(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 an inert atmosphere (N_2) glovebox. Absorption spectra were recorded on a Varian Cary 6000i UV-Vis-NIR

spectrophotometer within the NIR/visible spectral region (1600 $\geq \lambda \geq$ 400 nm) under several applied potentials.

In situ Conductivities. The conductivities of polymer films were determined using equation (1).¹ 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.

$$\sigma = \frac{\iota_D}{V_D} \times \frac{D}{n \cdot T \cdot L} \tag{1}$$

 Table S1. Crystal Data and Structure Refinement of 1.

Empirical formula	C27 H26 N2 O2 S2
Formula weight	474.62
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a (Å)	5.723
b (Å)	12.338
c (Å)	33.143
α (deg)	90
β (deg)	90
γ (deg)	90
Volume (Å ³)	2340.2
Ζ	4
ρ (mg/cm ³)	1.347
μ (mm ⁻¹)	0.256
F(000)	1000
Crystal size (mm)	0.31 x 0.05 x 0.03
θ (deg)	1.76 to 25.00
Index ranges	$-6 \le h \le 6$
	-14 ≤ k≤ 14
	$-39 \le l \le 39$
Reflections collected	19521
Max. and min. transmission	0.8918 and 0.7995
GOF on F^2	1.092
$R1, wR2 [I > 2\sigma(I)]$	0.0645, 0.1347
<i>R1, wR2</i> [all data]	0.0782, 0.1703
Largest diff. peak and hole (e.Å ⁻³)	0.322 and -0.396

 Table S2. Crystal Data and Structure Refinement of 11.

Empirical formula	C35 H28 N2 Ni O2 S4
Formula weight	695.54
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_{l}/c$
a (Å)	7.515
b (Å)	35.334
c (Å)	11.422
α (deg)	90
β (deg)	90.44
γ (deg)	90
Volume (Å ³)	3032.8
Ζ	4
ρ (mg/cm ³)	1.523
$\mu (\mathrm{mm}^{-1})$	0.953
F(000)	1440
Crystal size (mm)	0.15 x 0.08 x 0.03
θ (deg)	3.22 to 25.03
Index ranges	$-8 \le h \le 8$
	$-42 \le k \le 42$
	-13 ≤1 ≤ 13
Reflections collected	20776
Max. and min. transmission	0.9720 and 0.8703
GOF on F^2	1.069
$R1, wR2 [I > 2\sigma(I)]$	0.0570, 0.1187
<i>R1, wR2</i> [all data]	0.0852, 0.1331
Largest diff. peak and hole (e.Å ⁻³)	0.404 and -0.506

 Table S3. Crystal Data and Structure Refinement of 8.

Empirical formula	C74 H62 Co2 N6 O6 S8
Formula weight	1505.64
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_{l}/c$
a (Å)	8.9360(18)
b (Å)	11.6472(25)
c (Å)	31.5458(69)
a (deg)	90
β (deg)	93.753(3)
γ (deg)	90
Volume (Å ³)	3276.22(10)
Ζ	2
$\rho (\mathrm{mg/cm^3})$	1.526
μ (mm ⁻¹)	0.823
F(000)	1556
Crystal size (mm)	0.23 x 0.17 x 0.11
θ (deg)	2.18 to 25.00
Index ranges	$-10 \le h \le 10$
	$-13 \le k \le 13$
	$-37 \le 1 \le 37$
Reflections collected	58109
Max. and min. transmission	0.9149 and 0.8333
GOF on F^2	1.261
$R1, wR2 [I > 2\sigma(I)]$	0.0628, 0.1427
<i>R1, wR2</i> [all data]	0.0644, 0.1448
Largest diff. peak and hole (e.Å ⁻³)	0.764 and -0.865

 Table S4. Crystal Data and Structure Refinement of 5.

Empirical formula	C40 H38 N4 O4 S4 V
Formula weight	817.92
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	19.124
b (Å)	7.767
c (Å)	25.554
a (deg)	90
β (deg)	98.99
γ (deg)	90
Volume (Å ³)	3749.0
Ζ	4
$\rho (\mathrm{mg/cm^3})$	1.449
μ (mm ⁻¹)	0.536
F(000)	1700
Crystal size (mm)	0.19 x 0.13 x 0.06
θ (deg)	2.84 to 25.00
Index ranges	$-22 \le h \le 22$
	$-9 \le k \le 9$
	$-30 \le 1 \le 30$
Reflections collected	29463
Max. and min. transmission	0.9686 and 0.9051
GOF on F^2	1.032
$R1, wR2 [I > 2\sigma(I)]$	0.0900, 0.1928
<i>R1, wR2</i> [all data]	0.1870, 0.2472
Largest diff. peak and hole (e.Å ⁻³)	0.524 and -0.563

 Table S5. Crystal Data and Structure Refinement of 20.

Empirical formula	C60 H66 Cl2 N2 Ni O2 S6
Formula weight	1169.12
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_{l}/c$
a (Å)	8.868(2)
b (Å)	19.809(5)
c (Å)	33.077(9)
a (deg)	90
β (deg)	102.154(7)
γ (deg)	90
Volume (Å ³)	5680(2)
Ζ	4
ρ (mg/cm ³)	1.367
μ (mm ⁻¹)	0.701
F(000)	2456
Crystal size (mm)	0.22 x 0.20 x 0.17
θ (deg)	1.63 to 25.00
Index ranges	$-10 \le h \le 10$
	$-23 \le k \le 23$
	$-39 \le 1 \le 39$
Reflections collected	101640
Max. and min. transmission	0.8901 and 0.8611
GOF on F^2	1.155
$R1, wR2 [I > 2\sigma(I)]$	0.0945, 0.2359
<i>R1, wR2</i> [all data]	0.0980, 0.2444
Largest diff. peak and hole (e.Å ⁻³)	1.252 and -1.082

 Table S6. Crystal Data and Structure Refinement of 21.

Empirical formula	C59 H64 Cl0 Cu N2 O2 S6
Formula weight	1089.02
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	Pbcn
a (Å)	29.325(16)
b (Å)	20.484(11)
c (Å)	9.653(5)
α (deg)	90
β (deg)	90
γ (deg)	90
Volume (Å ³)	5798(5)
Ζ	4
$\rho (mg/cm^3)$	1.247
μ (mm ⁻¹)	0.634
F(000)	2292
Crystal size (mm)	0.20 x 0.05 x 0.04
θ (deg)	2.31 to 25.00
Index ranges	$-34 \le h \le 34$
	$-24 \le k \le 24$
	- 11 ≤ 1 ≤ 11
Reflections collected	81863
Max. and min. transmission	0.9751 and 0.8836
GOF on F^2	1.365
$R1, wR2 [I > 2\sigma(I)]$	0.1134, 0.3260
<i>R1, wR2</i> [all data]	0.1939, 0.3267
Largest diff. peak and hole (e.Å ⁻³)	0.657 and -0.485



Figure S1. Electropolymerization of ligand monomers: (A) **1**, (B) **2**, (C) **3**, and (D) **17**.³ Insets show the linear relationship between peak polymer oxidation/reduction currents and number of scans.



Figure S2. CV (red) and conductivity profile (blue) of ligand monomers: (A) poly-1, (B) poly-2, and (C) poly-3 measured in 0.1 M TBAPF₆/CH₂Cl₂ electrolyte solution. Scan rate 10 mV/s, 40 mV offset potential.



Figure S3. Scan rate dependence study of ligand polymers: (A) poly-1, (B) poly-2, and (C) poly-3.



Figure S4. Linear relationships of oxidative (black) and reductive (red) peak current versus scan rate of ligand polymers in 0.1 M TBAPF₆/CH₂Cl₂ electrolyte solution: (A) poly-**1**, (B) poly-**2**, and (C) poly-**3**.



Figure S5. Electropolymerization of metal complex monomers: (A) 5, (B) 8, (C) 11, (D) 14, (E) 18, (F) 19, (G) 20 and (H) 21. Insets show the linear relationship between peak polymer oxidation/reduction currents and number of scans.



Figure S6. CV (red) and conductivity profile (blue) of copper-containing metallopolymers (poly-**13**, poly-**14**, and poly-**21**) in 0.1 M TBAPF₆/CH₂Cl₂ electrolyte solution. Scan rate 10 mV/s, 40 mV offset potential.



Figure S7. CV (red) and conductivity profile (blue) of vanadium-containing metallopolymers (poly-4, poly-5, and poly-18) in 0.1 M TBAPF₆/CH₂Cl₂ electrolyte solution. Scan rate 10 mV/s, 40 mV offset potential.



Figure S8. CV (red) and conductivity profile (blue) of nickel-containing metallopolymers (poly-**10**, poly-**11**, and poly-**20**) in 0.1 M TBAPF₆/CH₂Cl₂ electrolyte solution. Scan rate 10 mV/s, 40 mV offset potential.



Figure S9. CV (red) and conductivity profile (blue) of cobalt-containing metallopolymers (poly-7, poly-8, and poly-19) in 0.1 M TBAPF₆/CH₂Cl₂ electrolyte solution. Scan rate 10 mV/s, 40 mV offset potential.



Figure S10. 1 H NMR Spectra (CDCl₃, 298 K) of compounds 11 (top) and 20 (bottom).



Figure S11. Normalized 2D spectroelectrochemical difference spectra of poly-1, poly-2, and poly-17 measured on ITO-coated glass in CH_2Cl_2 electrolyte solution at various applied potentials between 0 and 1.20 V vs Fc/Fc⁺.

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