

Electroactivity Enhancement by Redox Matching in Cobalt Salen-Based Conducting Polymers**

By Richard P. Kingsborough and Timothy M. Swager*

The preparation of polymer-modified electrodes that function as electrocatalysts, chemical sensors, and electrochromic displays remains an active field of research.^[1] We are currently engaged in the design of new conducting polymer architectures containing transition metals in well-defined coordination environments.^[2] Our interest in these materials is motivated by the wealth of desirable characteristics endowed by transition metals for the development of sensory materials that should be responsive to anions, Lewis bases, and small molecules (CO, O₂, NO, etc.).^[3,4]

Polymers based on transition metal-containing *N,N'*-ethylenebis(salicylideneimine) (salen) complexes have been previously prepared by the oxidative polymerization of monomeric M(salen) complexes.^[5] In all but a few of these polymers,^[5d,5j] the electrochemistry of the films displays ligand-based redox processes at high potentials that are considerably removed from the expected metal-based electroactivity. These films generally lacked metal-centered electroactivity; however, thin Co(salen) films did display redox processes attributed to the Co^{2+/3+} couple, which diminished as the films became progressively thicker.^[5d] We have targeted conducting polymers that incorporate the metal centers as part of the conduction pathway and tightly couple the conductivity to the redox characteristics of the metal center. We believe that an organic polymer redox potential that is the same or below that of the metal center should create materials with enhanced electron mobilities, and thereby form optimized sensory and catalytic materials. In this contribution we demonstrate that tuning the redox potential of the organic polymer backbone to be similar to that of the Co^{2+/3+} redox potential creates enhanced electroactivity of cobalt centers embedded in the polymer backbone. This intimate coupling of the metal and polymer in the conduction process can impart sensitivity to specific analytes, and we further demonstrate that Lewis bases such as pyridine and substituted pyridines affect the polymers' conductivity.

To generate the maximum interaction between thiophene moieties and the cobalt centers we designed salen complexes with a para relationship between phenolic oxygens and the thiophenes. The monomer ligands, **2** and **5**,

were produced by palladium-catalyzed Stille coupling methods (Scheme 1) followed by condensation with ethylenediamine.^[6a] Monomeric cobalt complexes **3** and **6** were prepared by standard methods^[6b] as black microcrystals from dimethylformamide (DMF) solutions under argon.

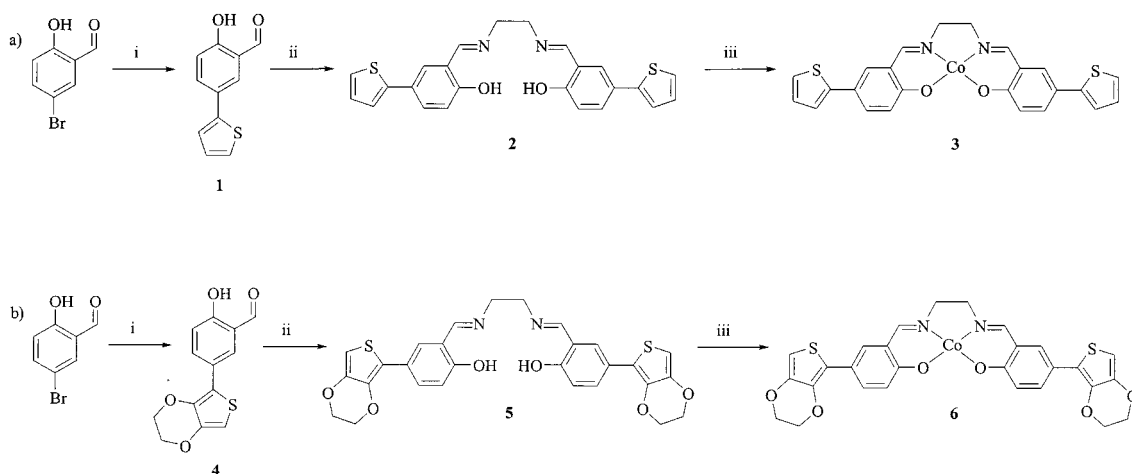
Polymeric films of **3** can be readily oxidatively deposited on platinum electrodes from a saturated monomer solution (**3**) ca. 0.1 mM in 0.1 M Bu₄NPF₆/MeCN by scanning between -0.75 V and 0.85 V (Fig. 1).^[7] The cyclic voltammogram (CV) of a very thin film of poly(**3**) reveals that the ratio of metal- to organic-centered redox waves is approximately 1:2 (Fig. 2a). Upon growing a film sufficiently thick to connect two interdigitated electrodes, we see that the wave attributed to the Co^{2+/3+} redox process is much smaller and a much more broad organic-based electrochemical process centered at 0.45 V is apparent, with a ratio of metal- to organic-centered redox waves of approximately 1:5 (Fig. 2b). The polymers display a broad, polythiophene-like CV trace, indicative of linear polymerization through the thiophene substituents, as shown in Scheme 2. The polymer structure was indirectly confirmed by scanning a number of related transition metal complexes of the methyl-terminated salen ligand, *N,N'*-ethylenebis(5-(5-methylthienyl)salicylideneimine), to the same polymerization potentials. The absence of any polymer deposition (Scheme 3) supports the proposed structure and similar results have been reported in studies concerning the oxidative polymerization of M(salen) complexes.^[5]

To account for the decreased electroactivity of the cobalt center in the thick films relative to the thin ones we postulate that when the polymer is in the reduced state it effectively acts as an insulator, preventing the Co^{2+/3+} redox process from occurring in the majority of the polymer structure. Those centers being oxidized or reduced are most likely to be very close to the electrode surface. We believe that the remaining cobalt centers are irreversibly oxidized to Co³⁺ during the polymerization process while the polymer is in its oxidized form, as it is more positive than the Co^{2+/3+} redox couple. This has been observed by Horwitz and Murray.^[8]

In situ conductivity experiments on 5 μm interdigitated microelectrodes^[9] (Fig. 2c) reveal a maximum drain current, which is proportional to conductivity, occurring at the same potential as the second polymer oxidation wave. Furthermore, poly(**3**) shows no detectable contribution to the overall conductivity from the metal-centered self-exchange process, consistent with what we have observed previously in copper-based polyrotaxanes in which the copper redox wave is well removed from the polymer redox waves.^[2a] Absolute conductivity values are difficult to calculate from our interdigitated devices, as we cannot readily determine what portion of the polymer lies on top of or between the interdigitated electrodes. Additionally, the coverage is not expected to be uniform since our surface coverages are much less than the interelectrode spacing. Clearly the polymer films must be extremely thin between

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Scheme 1. a) i) 2-Tributylstannylthiophene, cat. $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$, DMF, 80°C , 12 h, Ar, 55–60 %; ii) 0.52 equivalents ethylenediamine, benzene, RT, 12 h, 94 %; iii) $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, DMF, Ar, RT, 83 %. b) i) 2-Tributylstannyl-3,4-ethylenedioxythiophene, cat. $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$, DMF, 80°C , 12 h, Ar, 27 %; ii) 0.52 equivalents ethylenediamine, benzene, RT, 12 h, 94 %; iii) $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, DMF, Ar, RT, 83 %.

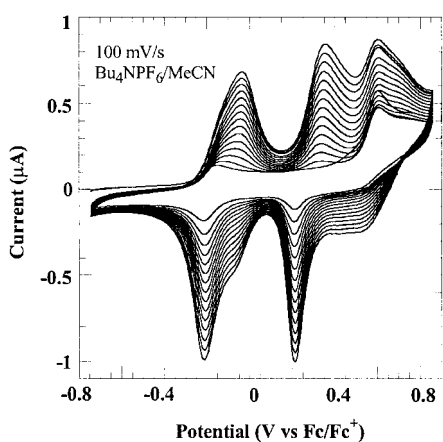


Fig. 1. Anodic polymerization of **3** on a platinum button electrode in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{MeCN}$ under a N_2 atmosphere at a scan rate of 100 mV/s. Potentials are referenced to the Fc/Fc^+ couple.

the electrodes. Zotti and co-workers^[10] have developed a method for determining conductivities of materials by a similar method and have used a standard material, poly(3-methylthiophene), for which the bulk conductivity is known (60 S cm^{-1}),^[11] to correct for non-uniform coverage. By this method we have determined poly(**3**) to have a conductivity of 40 S cm^{-1} .^[12,13]

From the conductivity studies it seems that although the cobalt center is an integral part of the poly(**3**) backbone it does not contribute to the overall conductivity. To confirm the importance of the metal centers to these systems we have attempted the oxidative polymerization of Schiff bases based on 5-(2-thienyl)-2-methoxybenzaldehyde (**7**). No film growth was observed in these systems. In fact, for this last compound the thiophene moieties are very resistant to oxidation, being oxidized at potentials similar to thiophene itself,^[14] thus emphasizing the metal-centered

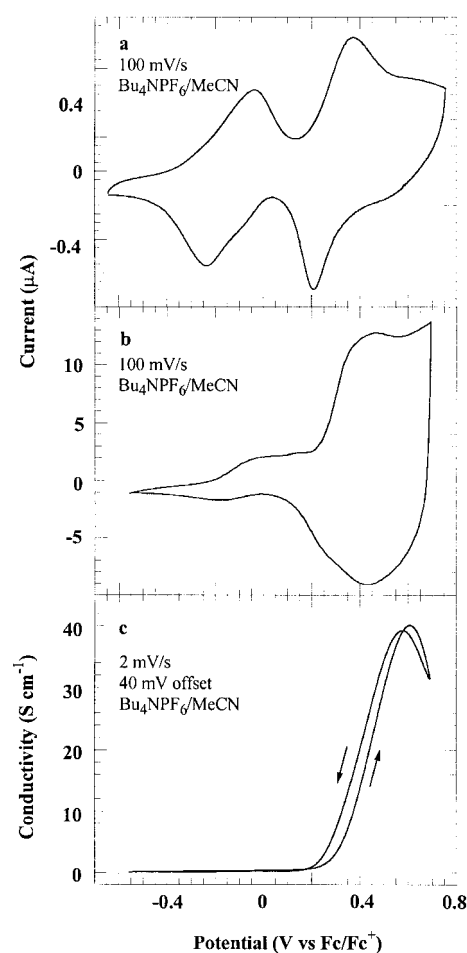
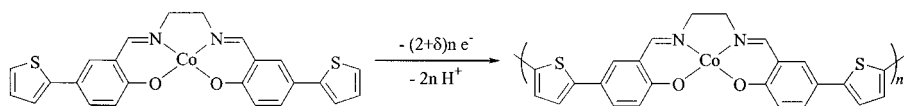
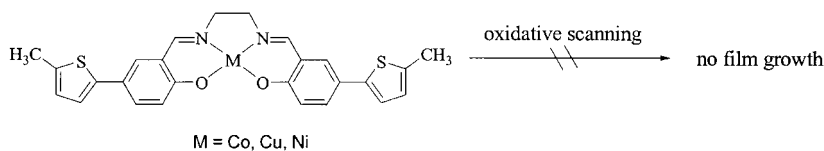


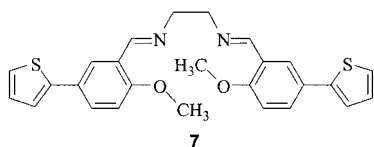
Fig. 2. a) Cyclic voltammogram of a thin film of poly(**3**) in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{MeCN}$ on a platinum button electrode. b) Cyclic voltammogram of poly(**3**) on an interdigitated microelectrode with $5 \mu\text{m}$ spacing. c) Conductivity versus electrochemical potential of the same sample of poly(**3**) as in (b) on interdigitated microelectrodes.



Scheme 2.



Scheme 3.



conjugation in these monomers and polymers. From the relatively low oxidation potential displayed by **3** with respect to **7**, it seems that **3** behaves similar to an oligothiophene as regards its oxidation behavior.

In previous studies of transition metal-containing polymers,^[2c] we have found that using an EDOT-based (where EDOT stands for 3,4-ethylenedioxythiophene) organic polymer backbone leads to an overall decrease of the polymer oxidation potential. Thus, we redesigned our polymer such that the oxidation potentials of the cobalt and the organic backbone would at least partially overlap. Electrochemical polymerization (Fig. 3) of saturated solutions of **6**

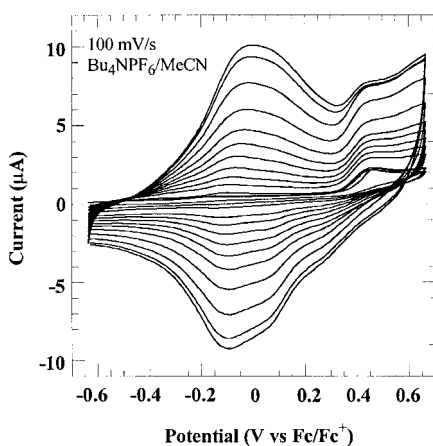


Fig. 3. Anodic polymerization of **6** on an interdigitated microelectrode with 5 µm spacing in 0.1 M Bu₄NPF₆/MeCN at a scan rate of 100 mV/s.

(**6** ca. 0.1 mM) immediately reveals the benefits of the more electron-rich polymer backbone. As can be seen in Figure 4a, the redox potential of the poly(**6**) backbone has been significantly lowered to almost perfectly coincide with the Co^{2+/3+} redox wave. Close inspection of the CV trace reveals that there are two redox waves seen at -0.11 V and 0.07 V, due to the Co^{2+/3+} and polymer redox processes, respectively. The identity of the Co^{2+/3+} wave was revealed by the addition of pyridine (Fig. 4a), resulting in a shift of the wave at -0.11 V to lower potential (-0.38 V), consistent

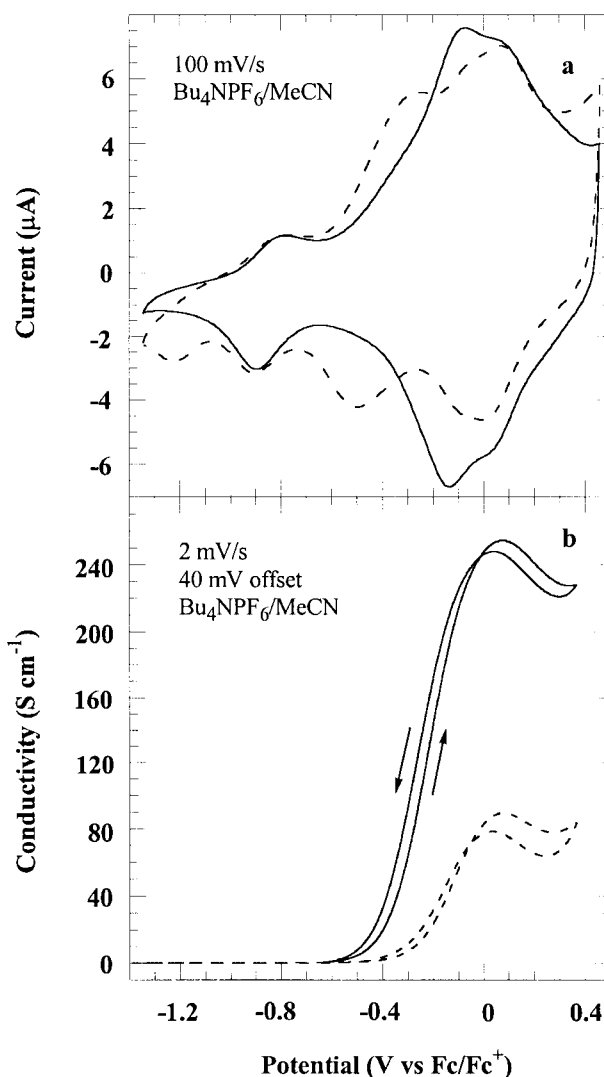


Fig. 4. a) Cyclic voltammogram of poly(**6**) on a platinum button electrode in 0.1 M Bu₄NPF₆/MeCN (solid line) and in the presence of 40 mM pyridine/0.1 M Bu₄NPF₆/MeCN (dashed line), illustrating the presence of the cobalt-based redox wave. b) Conductivity versus electrochemical potential of poly(**6**) on an interdigitated microelectrode before (solid line) and after (dashed line) exposure to pyridine.

with shifts observed in monomeric systems.^[15] Also observed in the cyclic voltammogram at lower potentials (-0.84 V) is a wave that has been assigned to the Co^{+2/+} re-

dox transition. In a similar fashion to poly(**3**) films, it appears that only a small fraction of the cobalt centers can undergo this additional redox process in the thicker films. The conductivity of the poly(**6**) film on interdigitated microelectrodes shows a broad trace increasing from ca. -0.4 V through a maximum at 0.05 V and a subsequent decrease to a high plateau at higher potentials (Fig. 4b). Conductivity values^[13] calculated using poly(3-methylthiophene) as a standard are quite high, ca. 250 S cm^{-1} , roughly equal to that of poly(EDOT).^[12]

The anodic polymerization of **3** was also carried out in $0.1 \text{ M Et}_4\text{NPF}_6$ electrolyte solutions in order to determine whether cation transport through the film was affecting the electroactivity of the $\text{Co}^{2+/3+}$ redox wave. In this case, there is a significant enhancement of the $\text{Co}^{2+/3+}$ wave relative to the polymer-based waves, even in films sufficiently thick to connect the microelectrodes. This may be due to an enhanced transport of the smaller cation or an overall morphological difference between the films grown in different electrolytes that allows all of the cobalt centers to undergo reversible redox processes while in the insulating regime of the polymer backbone. While the exact nature of this enhancement is unknown, it appears that films of poly(**3**) are sensitive to the electrolyte used in the film synthesis. Similar studies of the redox-matched system, poly(**6**), showed no difference in the cyclic voltammograms when grown in either Et_4NPF_6 or Bu_4NPF_6 . These results reinforce our original premise that for these materials to have useful electrocatalytic and sensory applications, the passivation of the $\text{Co}^{2+/3+}$ redox wave must be overcome. Enhancement of the electroactivity that is observed for poly(**6**) in either electrolyte system shows that this material's activity is not subject to the conditions in which the polymer was synthesized, as is the case for poly(**3**).

Spectroelectrochemical measurements of both polymers on indium tin oxide (ITO) glass electrodes were performed to elucidate the conduction mechanism. In their reduced forms, the polymers display broad absorptions in the visible region with $\lambda_{\text{max}} = 432 \text{ nm}$ for poly(**3**) and 488 nm for poly(**6**), comparable to those observed by Goldsby in polymers of $\text{Cu}(\text{salen})$ and $\text{Ni}(\text{salen})$.^[5a] As the polymers are oxidized, this absorbance shifts to higher energy and rapidly decreases in intensity. Concurrent with this shift is the formation of two new peaks at lower energy, which extend into the near IR and are often considered to be the signature of free carriers in the metallic state.^[16] This type of behavior has also been observed in purely organic conducting polymer systems.^[9c,9d,16,17]

Exposure of the polymers to pyridine (ca. 40 mM) results in an irreversible, approximately 66% quenching of the conductivity of poly(**6**) (Fig. 4b). Rinsing the polymer with fresh electrolyte did not result in a restoration of the original conductivity. Addition of 2,6-lutidine also results in the same film behavior. While no conductivity studies have been performed, others have observed that exposure of pyridine to transition metal-based polymer systems results

in the complete, but reversible, passivation of the electrode surface.^[5] Electrochemistry in the presence of the sterically more encumbered 2,6-di-*tert*-butylpyridine also resulted in a small decrease (ca. 10%) in polymer conductivity. However, unlike with lutidine, the conductivity of the polymers can be restored upon rinsing with fresh electrolyte. These results tend to suggest that there is a significant interaction of these Lewis bases with the cobalt centers in both oxidation states and that the Co^{2+} centers remain five-coordinate after reduction. However, at present we cannot rule out interactions of the pyridine with the organic portion of the polymer backbone.

In summary, we have synthesized conducting polymer-transition metal hybrid materials that display high conductivity and a high sensitivity to coordinating ligands. We have found that by controlling the oxidation potential of the polymer relative to that of the metal center, the overall electrochemical properties of the polymer can be varied. Our future studies will seek to address the roles of the metal center and the electrolyte in the conduction properties, provide a further elucidation of the conduction mechanism, as well as further the development of potential sensory and catalytic applications.

Experimental

5-(2-Thienyl)salicylaldehyde (1): To a mixture of 5-bromosalicylaldehyde (2.847 g , 14.16 mmol) and $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$ (0.497 g , 0.708 mmol , 0.05 equiv.) was added tributylstannyl thiophene (6.75 mL , 21.24 mmol , 1.5 equiv.) in 25 mL of DMF. The reaction mixture was heated at 80°C for 16 h , over which time the reaction color changed from light yellow to dark red. The reaction was cooled, diluted with Et_2O , and washed with dilute NH_4Cl ($4 \times 150 \text{ mL}$). The organic layer was collected and filtered through a short silica pad to yield a yellow filtrate. The solvent was removed under reduced pressure to afford a gummy yellow solid, which was transferred to a frit and washed with hexanes. The yellow solid was dried in vacuo to afford 1.895 g (9.28 mmol , 66%) of a yellow powder (m.p. $102\text{--}103^\circ\text{C}$). $^1\text{H NMR}$ (250 MHz , CDCl_3) δ 11.01 (s, 1H), 9.96 (s, 1H), $7.80\text{--}7.76$ (m, 2H), $7.29\text{--}7.24$ (m, 2H), 7.09 (dd, 1H, $J = 3.8$ and 5.1 Hz), 7.04 (dd, 1H, $J = 2.5$ and 7.0 Hz). $^{13}\text{C NMR}$ (62 MHz , CDCl_3) δ 196.5 , 161.1 , 142.7 , 134.7 , 130.8 , 128.3 , 127.1 , 124.8 , 123.0 , 120.8 , 118.4 . UV-vis (MeCN) λ_{max} 210 , 252 , 289 , 361 nm . MS m/z 204 (M^+). HRMS (FAB) found m/z 205.0324 ($[\text{M} + \text{H}]^+$); calcd. for $\text{C}_{11}\text{H}_9\text{O}_2\text{S}$ m/z 205.0323 ($[\text{M} + \text{H}]^+$). Elemental anal. calcd. for $\text{C}_{11}\text{H}_9\text{O}_2\text{S}$: C, 64.69 ; H, 3.95 . Found: C, 64.76 ; H, 3.78 .

5-(2-(3,4-Ethyleneedioxy)thienyl)salicylaldehyde (4): This compound was prepared in a similar fashion to **1** except that 2-tributylstannyl-3,4-ethylene-dioxythiophene was used in place of thiophene (27%). m.p. 132°C , dec. $^1\text{H NMR}$ (250 MHz , CDCl_3) δ 10.98 (s, 1H), 9.94 (s, 1H), 7.92 (d, 1H, $J = 2.3 \text{ Hz}$), 7.84 (dd, 1H, $J = 2.4$ and 8.7 Hz), 7.00 (d, 1H, $J = 8.7 \text{ Hz}$), 6.29 (s, 1H), $4.34\text{--}4.25$ (m, 4H). $^{13}\text{C NMR}$ (125 MHz , CDCl_3) δ 197.1 , 160.4 , 142.6 , 138.2 , 134.9 , 131.1 , 125.9 , 120.8 , 118.2 , 115.8 , 97.5 , 65.1 , 64.7 . UV-vis (MeCN) λ_{max} 214 , 257 , 295 , 373 nm . MS m/z 262 (M^+). HRMS (FAB) found m/z 263.0378 ($[\text{M} + \text{H}]^+$); calcd. for $\text{C}_{13}\text{H}_{11}\text{O}_4\text{S}$ m/z 263.0378 ($[\text{M} + \text{H}]^+$). Elemental anal. calcd. for $\text{C}_{13}\text{H}_{11}\text{O}_4\text{S}$: C, 59.53 ; H, 3.84 . Found: C, 59.35 ; H, 3.86 .

The ligands [6a] and metal complexes [6b] were prepared by literature procedures from the appropriate salicylaldehyde.

***N,N'*-Ethylenebis(5-(2-thienyl)salicylideneimine) (2):** 94% yellow powder, m.p. 255°C , dec. $^1\text{H NMR}$ (250 MHz , CDCl_3) δ 13.29 (s, 2H), 8.43 (s, 2H), 7.55 (dd, 2H, $J = 2.4$ and 8.4 Hz), 7.46 (d, 2H, $J = 2.3 \text{ Hz}$), $7.22\text{--}7.16$ (m, 4H), 7.05 (dd, 2H, $J = 3.6$ and 5.0 Hz), 6.97 (d, 2H, $J = 8.7 \text{ Hz}$), 3.99 (s, 4H). The poor solubility of this compound prevented characterization by $^{13}\text{C NMR}$ spectroscopy. UV-vis (MeCN) λ_{max} 252 , 293 nm . MS m/z 432 (M^+). HRMS (EI) found m/z 432.0964 (M^+); calcd. for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2\text{S}_2$ (M^+) 432.0966 . Elemental anal. calcd. for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2\text{S}_2$: C, 66.64 ; H, 4.66 ; N, 6.48 . Found: 66.43 ; H, 4.35 ; N, 6.34 .

N,N'-Ethylenebis(5-(2-(3,4-ethylenedioxy)thienyl)salicylideneimine) (**5**): 94 % yellow solid, m.p. 245 °C, dec. ¹H NMR (250 MHz, CDCl₃) δ 13.26 (s, 2H), 8.41 (s, 2H), 7.63–7.60 (m, 4H), 6.95 (d, 2H, *J* = 8.3 Hz), 6.22 (s, 2H), 4.35–4.22 (m, 8H), 3.97 (s, 4H). The poor solubility of this compound prevented characterization by ¹³C NMR spectroscopy. MS *m/z* 549 ([M + H]⁺). HRMS (FAB) found *m/z* 549.1157 ([M + H]⁺); calcd. for C₂₈H₂₅N₂O₆S₂ *m/z* 549.1154 ([M + H]⁺).

N,N'-Ethylenebis(5-(2-thienyl)salicylideneiminato)cobalt(II) (**3**): 83 % black microcrystalline solid, m.p. >250 °C. UV-vis (MeCN) λ_{max} 261, 315, 389, 415 nm. MS *m/z* 489 (M⁺). HRMS (EI) found *m/z* 489.0144 (M⁺); calcd. for C₂₄H₁₈CoN₂O₂S₂ (M⁺) 489.0142. Elemental anal. calcd. for C₂₄H₁₈CoN₂O₂S₂: C, 58.89; H, 3.71; N, 5.72. Found: C, 58.76; H, 3.94; N, 6.11.

N,N'-Ethylenebis(5-(2-(3,4-ethylenedioxy)thienyl)salicylideneiminato)cobalt(II) (**6**): 83 % green-black microcrystalline solid, m.p. >250 °C. UV-vis (MeCN) λ_{max} 267, 317, 398 nm. HRMS (LDMS) found *m/z* 605.02 (M⁺); calcd. for C₂₄H₁₈CoN₂O₂S₂ (M⁺) 605.54. Elemental anal. calcd. for C₂₈H₂₂CoN₂O₆S₂: C, 55.54; H, 3.66; N, 4.63. Found: C, 54.73; H, 3.67; N, 4.56.

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the polymer thickness; with a 5 μm gap, *D*; *n* = 99 gaps; and a 0.49895 cm electrode length, *L*.

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

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Superlattice Structures in Poly(phenylenevinylene)-Based Self-Assembled Films**

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Several years ago, Decher and co-workers presented a new layer-by-layer self-assembly method to fabricate polymeric films consisting of layers of different polymers.^[1,2] These multilayer structures are prepared by alternate dipping of a charged substrate into an aqueous solution of a positively charged polyelectrolyte and another solution of a negatively charged polyelectrolyte; the adsorption of alternate layers is driven by electrostatic interactions. In this way layered multicomposites with multifunctional properties can be built, which are of interest for various electro-optical applications. The method was applied successfully to fabricate light-emitting devices (LEDs) in which the emitting layer is derived from the semiconducting conjugated polymer poly(*p*-phenylenevinylene) (PPV).^[3–7] The fabrication of multifunctional devices requires highly ordered and stable multilayer systems in which the different layers have different functionalities. It is important, therefore, to control and minimize the interpenetration of the different polymers at the interfaces (buried interfaces) such that the polymer penetration depth will not exceed 1–2 nm. This interpenetration depth at the interface is directly related to the interlayer roughness.

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