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Electronic interactions in metallated polythiophenes: what can be learned from model complexes

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Contents

Abstract

Conjugated polymers containing metal centers are an important class of new materials due to the coupling of the chemical, optical, and electronic properties of the metal moiety to those of the polymer. Conjugated polythiophene derivatives have been extensively explored due to their chemical stability and synthetic accessibility. Bimetallic model complexes in which the two metals are bridged by a conjugated oligothiophene provide an approach to understanding the properties of these materials. The electronic interactions between the metals in these complexes can be examined, and provide insight into coupling between analogous complexes tethered to polythiophenes. In this review such model systems are surveyed, along with some of the metal-containing polythiophene derivatives that have been prepared.

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Keywords: Polythiophene; Conjugated polymers; Intervalence charge transfer; Cyclic voltammetry

1. Introduction

Conjugated polymers have been extensively studied over the last few decades due to their fascinating electronic properties, which from the time of their original discovery suggested that these materials could be useful for many different applications [1]. With the discovery in the early 1990s of electroluminescence in conducting polymers [2] rapid development of devices using these materials occurred [3] and companies around the world are now developing displays for cell phones and computers utilizing this technology [4]. The drive towards ever-smaller computer

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technologies has also spurred research in the use of molecular materials such as conjugated polymers in nanosized devices. Although many challenges remain before the viability of this approach is known, it is clear that research in this field is burgeoning and of great current interest.

Although the vast majority of conjugated polymers that have been made are based on purely organic backbones [1] recently several groups around the world have been examining the possibility of incorporating metal complexes into these materials. The driving force for this work lies in the possibility of coupling the chemical, optical, and electronic properties of metal complexes to those of the polymer backbone, thus accessing novel materials with new properties. A key concern in this field is determining the nature and extent of the electronic coupling between the metal and conjugated backbone units, therefore, much attention has been focused on building and studying model complexes in which metal groups are tethered to conjugated fragments via different linkages, and studying the nature of the coupling in these systems. In this review, we survey both model complexes and some of the polymers that have been made, focusing on one type of organic backbone—polythiophene.

2. Polythiophenes and conjugated polymers

Conjugated polymers are materials in which a backbone of alternating single and multiple bonds result in π-conjugation by overlap of the π-orbitals, giving rise to a continuum of energy states called a band structure. Several common backbone structures are shown in Fig. 1, and many other derivatives based on these backbones have been investigated. An interesting property of conjugated polymers is that they can be doped using oxidizing agents resulting in large increases in the electronic conductivity of the polymer. Investigations have focused on understanding the nature of the charge carriers involved in conductivity, and the involvement of polarons (radical cations), bipolarons (dications) and neutral solitons (radicals) has all been examined. In addition to charge transport along single polymer chains, interchain transport is also important [5].

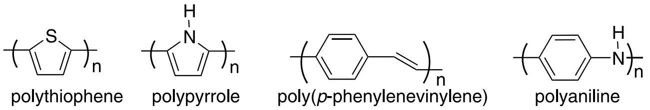


Fig. 1. Representative conjugated polymers.

3. Metallated polythiophenes

Metals can be incorporated into polythiophene backbones either as electronically isolated pendant groups (Fig. 2, Type I), electronically coupled pendant groups (Type II), or inserted into the conjugation path (Type III) [6]. Due to the interruption of the π-conjugation in Type III materials, the influence of the metal group in these materials is generally more significant than in Type II materials, where the metal may only indirectly affect the conjugated backbone via a combination of steric and inductive effects. Several reviews have summarized recent advances in the synthesis and characterization of this class of materials [6–8]; here we focus on the use of model complexes to understand the optical and electronic behavior of metallated polythiophenes.

The interaction between two adjacent metal groups via a conjugated polymer backbone can be difficult to study. The most useful probes of such interactions are spectroscopies and electrochemistry (discussed in more detail in Section 4), but many of the diagnostic measures of metal–metal interaction are lost or difficult to observe in polymers. This is because disorder, conformational effects

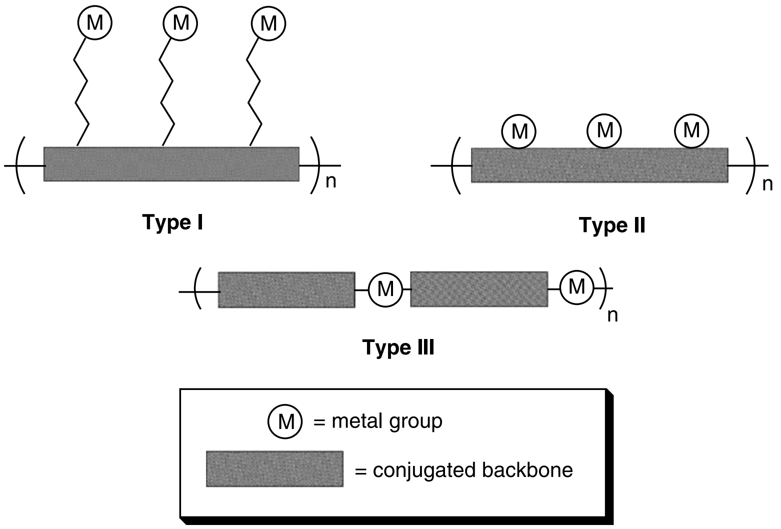


Fig. 2. Three types of metal-containing conjugated polymers.

and multiple environments cause spectral broadening and additional electrochemical features preventing proper assignment and interpretation. For this reason, many workers have carefully constructed model systems in which metal–metal, and metal–oligomer, interactions can be observed in a well-defined chemical environment.

4. Model systems

Metal–metal coupling has been studied in many bimetallic complexes using a variety of techniques [9]. Electrochemical methods (principally cyclic voltammetry or CV) allow determination of the redox potentials of two metal centers in a molecule. Interactions between metal sites result in increased separation in redox potentials (ΔE), due to stabilization of the mixed valent species that forms upon oxidation of one of the two metals. When ΔE is larger than the theoretically expected value in non-interacting systems ($\Delta E = 36$ mV), electronic interactions between the metals are likely. Electrostatic interaction between metal groups can also result in $\Delta E > 36$ mV, thus this is not a conclusive indication of interaction involving the bridging group [10].

Electronic spectroscopy on mixed-valent species (generated either via chemical oxidation or electrochemically) can show absorptions resulting from transitions from a ground-state configuration with one of the metals oxidized to a vibrationally excited state with the other metal oxidized. Such intervalence transitions may be interpreted with the theory originally developed by Hush [11] and allow determination of an effective electronic coupling parameter, V_{ab}:

$$V_{ab} = \frac{2.06 \times 10^{-2}}{R} (\varepsilon_{max} \bar{\nu}_{max} \Delta \bar{\nu}_{1/2})^{1/2}$$

Here, R is the donor–acceptor charge-transfer distance, ε_{max} is the extinction coefficient, $\bar{\nu}_{max}$ is the transition energy, and $\Delta \bar{\nu}_{1/2}$ is the full width at half-maximum in cm^{-1}. A related measure, the degree of mixing (α), is also used:

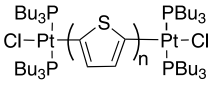
$$\alpha = \frac{V_{ab}}{\bar{\nu}_{max}}$$

Complexes have been categorized according to the classification system of Robin and Day [12]. Class 1 complexes ($\alpha = 0$) have non-interacting metal centers, Class 2 ($0 < \alpha < \sqrt{}2$) are weakly interacting, and Class 3 ($\alpha = \sqrt{}2$) are strongly interacting or completely delocalized. Other methods that have been used to probe metal–metal interaction include ESR, NMR, Mössbauer and magnetic measurements [9].

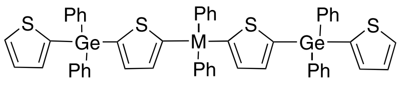
The following sections describe examples of model complexes in which the metals are bridged by an oligothiophene fragment, and some metallated polythiophenes categorized according to the type of linkage between the metal and conjugated moiety.

4.1. Direct M–C bonded

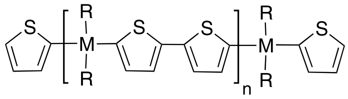
In the early 1990s Sonogashira and co-workers synthesized two Pt complexes (**1**) in which the metal centers were bridged by σ-bound thiophene [13]. The synthetic route to these complexes involved either tin–metal exchange using trimethylstannyl substituted thiophene and bithiophene precursors, or reaction of lithiothiophene derivatives with Pt–halide precursors. The electronic spectra of these bridged complexes showed some indication of increased conjugation due to red-shifts in the metal-to-ligand charge transfer (MLCT) bands.



1 n=1,2



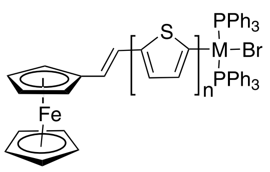
2 M = Si, Sn



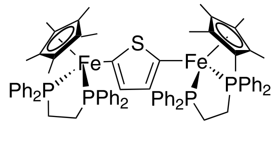
3 R = Bu, Ph;
M = Ge, Sn

Complexes containing Ge, Si and Sn (**2**) bridged by thiophene and bithiophene units have been prepared [14]. Some of these have also been elaborated to low molecular weight polymers such as **3**. These materials are slightly colored, with absorption in the 250–330 nm region, and are insulating in the neutral form. Doping with a nitrosonium salt results in the appearance of lower energy bands in the electronic spectrum, which are possibly due to intra-gap states.

Lin and co-workers have prepared several ferrocenyl capped Pd(II) and Pt(II) complexes (**4**) with thiophene spacers [15]. These were obtained by oxidative addition of bromothiophenes to zerovalent metal precursors giving σ-bonded complexes. In CV of these complexes the Fe(II)/(III) couple is shifted negative due to delocalization of Pd/Pt electron density over the bridge. The π → π* absorption bands for these complexes also show red-shifts attributable to additional charge-transfer character. The thiophene-bridged diiron complex **5** was prepared from a diacyl precursor via photochemical substitution with diphenylphosphinoethane [16]. CV of this species showed a significant degree of metal–metal interaction ($\Delta E = 550$ mV).



4 M = Pt, Pd
n = 1, 2



5

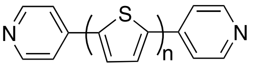
4.2. Imine complexes

4.2.1. Pyridines, bipyridines, and terpyridines

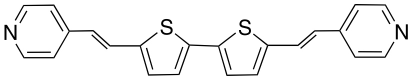
Pyridines, bipyridines and terpyridines are useful as ligating groups for various reasons: they form stable complexes with many metals, notably ruthenium, which are often stable in a variety of oxidation states, allowing access to mixed valence complexes. The synthesis of metal pyridine complexes is well established and straightforward, as is the synthesis of the ligands. Pyridines may also extend the delocalization of the conjugated thiophene bridge to the metal center.

Various pyridyl-capped oligothiophenes have been synthesized. For example, **6–9** [17] were synthesized via $Pd(PPh_3)_4$ catalyzed coupling reactions with trialkylstannylthiophenes and bromopyridine. A similar ligand containing ethylene spacers between the pyridine and the thiophene core (**10**) was synthesized via Heck coupling, and all these ligands were then complexed to Mo(Tp*) (Tp* = tris(3,5-dimethylpyrazol-1-yl)hydroborate). The Mo complexes of **6–8** showed evidence of metal–metal interaction via CV ($\Delta E = 270$, 220, and 160 mV, respectively) upon reduction. In all of these complexes both unpaired electrons are coupled to both Mo nuclei, as observed by ESR spectroscopy. The emission intensity of these complexes is lower then that of the corresponding free ligands due to quenching by the metal, and the $\pi \rightarrow \pi^*$ transition of the ligand is red-shifted upon complexation indicating some metal–bridge interaction. Compound **6** was also synthesized with 2,5-dibromothiophene and 4-(trimethylstannyl)pyridine in higher yield [18] and the di(pentaamineruthenium) complex prepared. While only a single oxidation peak was seen in the CV, an intervalence charge transfer (IVCT) band appears at 985 nm ($\varepsilon = 410$ mol^{-1} L cm^{-1}, $V_{ab} = 240$ cm^{-1}) upon formation of the mixed valence species by oxidation with KI. The value of V_{ab} is very similar for this complex and the dipyridyl 1,3-butadiene bridged analog indicating similar abilities of these ligands to facilitate interactions.

The organic bridge in **11** [19] was synthesized via cross coupling of 2,5-dibromothiophene and ethynylpyridine in the presence of CuI and $PdCl_2(PPh_3)_2$. The CV showed no evidence of metal–metal interaction but the luminescence of the complex is quenched relative to the free ligand.



6 n=1
7 n=2
8 n=3
9 n=4



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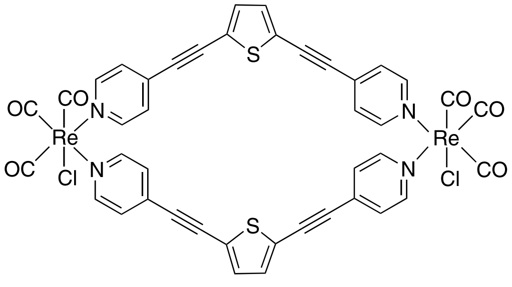
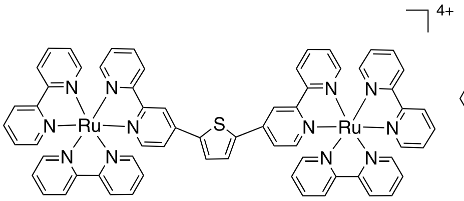


11

Ruthenium coordination compounds incorporating bipyridine (bpy) ligands have been extensively studied, and have well understood electrochemical and optical properties [20–22]. These ligands are also relatively easy to synthesize using heteroaromatic cross-coupling reactions. For these reasons, bipyridine has been incorporated into oligomeric complexes and polymers. For example, the bridging ligands in **12–14** [23] were synthesized by Stille coupling, using bis-stannylated oligothiophenes and 4-bromo-2,2′-bipyridine. The $\pi \rightarrow \pi^*$ absorptions for these ligands are red-shifted with respect to the unsubstituted thiophene core, which indicates delocalization onto the pyridine rings. In the complexes the $\pi \rightarrow \pi^*$ bands also appear red-shifted, but in **13** and **14** this band overlaps with the Ru → bpy MLCT and was, therefore, difficult to distinguish. No electrochemical coupling was observed, and the mixed valence species was not investigated.

The synthesis of the conjugated bridges of **15** and **16** [24] was accomplished in one step via a two-phase reaction of a propargylic alcohol derivative of thiophene and bromo or dibromobipyridine. Delocalization in the ligand was observed in the electronic spectra, but the metal groups did not show any interaction by CV. The synthesis of polymer **17** [25,26] was attempted via two routes: (1) Stille coupling of 3,4′,4‴,4‴′-tetraoctyl-5,5‴-bis(trimethylstannyl)quaterthiophene and 5,5′-dibromobipyridine and subsequent complexation, and (2) copolymerization of the stannyl tetrathiophene and metallated bromobipyridine monomer. The first method resulted in a high molecular weight polymer ($M_w = 67\,000$ g mol^{-1}), yet attempts to metallate this polymer were unsuccessful. The second method gave lower MW polymers ($M_w = 27\,000$ g mol^{-1}). No metal–metal interaction was observed electrochemically. A series of bipyridine–bithiophene ligands (**18**–**20**) were also synthesized via Stille coupling of stannyl bithiophene and the appropriate bromobipyridine, [27] and UV–visible spectra and electrochemistry of the free ligands indicate conjugation of the thiophene and the pyridine fragments. The ligands were then complexed to Ru, and the metal complexes and the free ligands were electropolymerized to form conducting films. The conductivity of the ruthenium containing films was found to be higher than that of the unmetallated films.



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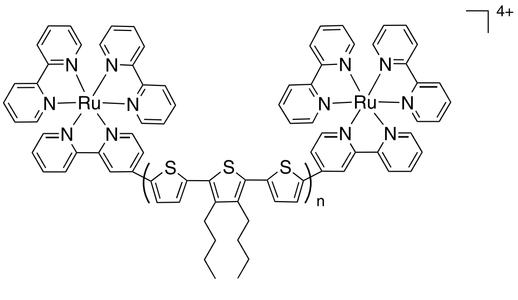
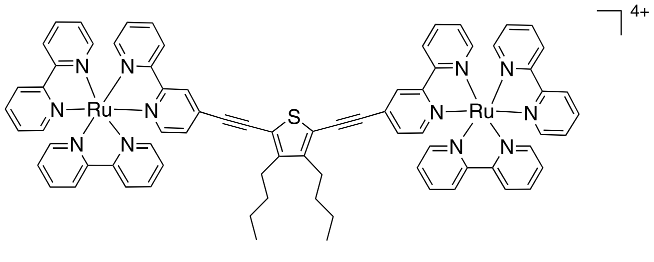


13 n=1
14 n=2



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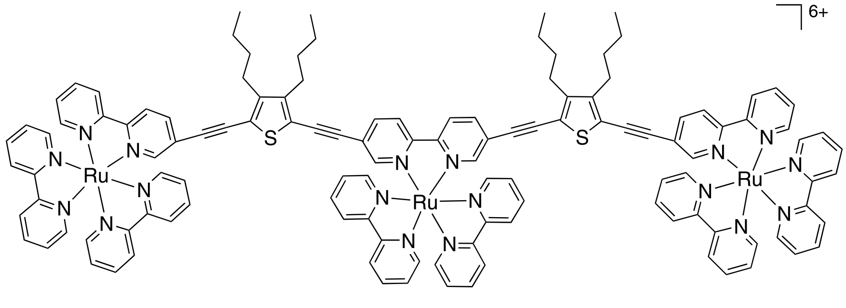

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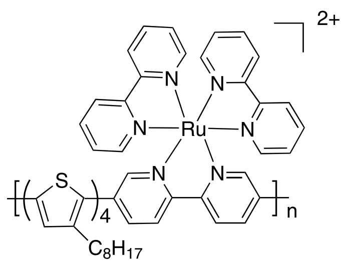

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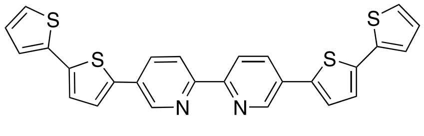

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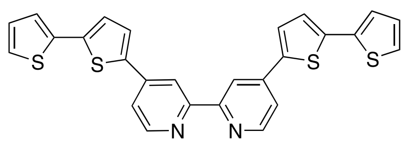

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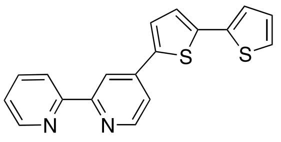

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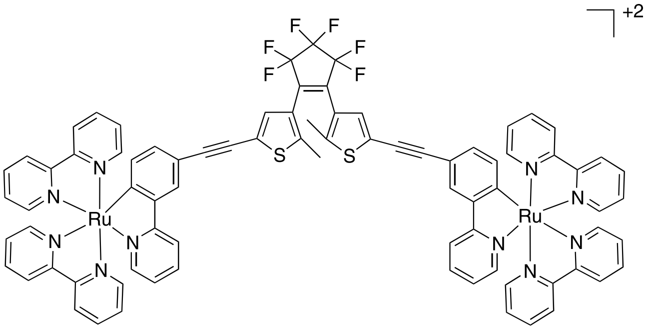

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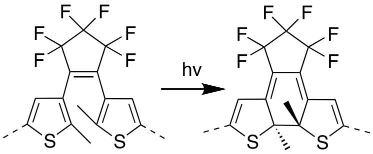
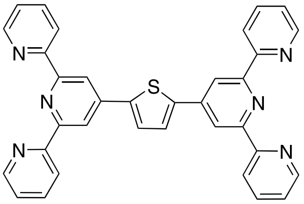


Scheme 1.

An interesting use of metal–metal coupling over a conjugated bridge is the photochromic switch **21** [28]. Complex **21** was synthesized via Pd-catalyzed coupling of the acetylene substituted ruthenium tris(bipyridine) unit and the iodonated dithienylethene fragment. Dithienylethene is photochromic, switching from open to closed forms upon irradiation with light (Scheme 1). The open form is not conjugated, but the closed form is, and incorporation of this into a bimetallic system leads to switchable coupling of the metal centers. The CV of both the open and closed forms exhibit a single reversible Ru oxidation wave, however, upon oxidation to the mixed valence state of the closed form an IVCT band was observed in the near-IR (1350 nm, $\varepsilon = 1400$ mol^{-1} L cm^{-1}, $V_{ab} = 200$ cm^{-1}).

Interestingly, the addition of the thiophene ring to the terpyridine ligating group raises the luminescence lifetime and efficiency over that of $[Ru(terpy)_2]^{2+}$, due to increased conjugation of the ligand. Also, the MLCT band red-shifts, ε increases, and luminescence lifetime and efficiency increase as the number of metal nuclei increases. This indicates a stabilization of the MLCT levels through metal–metal communication. In the mixed ruthenium–osmium complexes, energy transfer between the metal centers is observed via time-resolved luminescence experiments. All of these complexes exhibited one Ru(II)/Ru(III) oxidation process in the CV. A Ru complex of **23** was electropolymerized to yield a conducting thin film, [31] but no metal–metal interaction was observed by CV.



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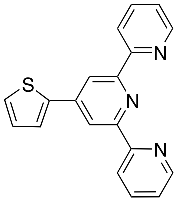

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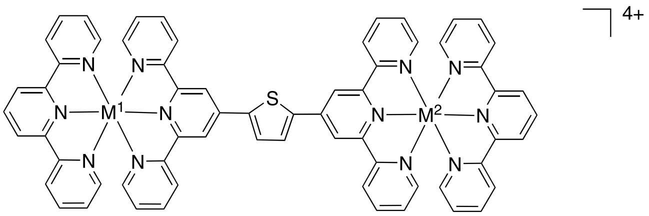
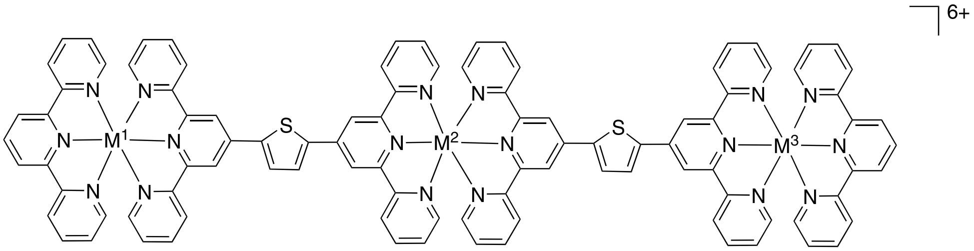


24 $M^1=M^2=Ru$
25 $M^1=M^2=Os$
26 $M^1=Ru$, $M^2=Os$



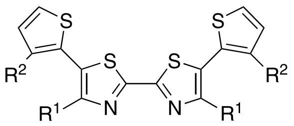
27 $M^1=M^2=M^3=Ru$
28 $M^1=M^3=Ru$, $M^2=Os$

A problem with the use of the chiral ruthenium tris-bipyridine end group is the formation of diastereomers, and so terpyridine (terpy) is an attractive alternative for building multinuclear achiral ruthenium complexes. A series of ruthenium and osmium complexes were synthesized using ligands **22** and **23** [29,30]. Ligands **22** and **23** were synthesized by condensation of 2-acetylpyridine and 2- or 2,5-thiophenecarbaldehyde, followed by a ring-closing reaction to form the central pyridine. Complexation to Ru and Os, with varying molar ratios, resulted in **24**–**28**.

4.2.2. Thiazoles

Thiazoles are interesting as ligating groups because they incorporate both an imine binding site and a five-membered sulfur-containing ring analogous to thiophene. Compound **29** was synthesized by two different routes: Stille coupling of stannylbithiazole and bromothiophene [32] and Suzuki coupling of 5,5′-dibromo-2,2′-bithiazole and 2-thienylboronic acid [33]. Compounds **30** and **31** were synthesized via Negishi coupling [33]. Biathiazole **29** was electropolymerized and coordinated to $Re(CO)_3Cl$ and $Re(CO)_3CH_3CN$

[32]. The MLCT band in the polymers is red-shifted with respect to the monomer complexes, due to more extended conjugation. The conductivity of the metallated polymers was three orders of magnitude lower than the free polymer, yet oxidation of the polymer did affect the electron density at the Re group, as observed through shifts in the infrared CO stretching frequency upon oxidation of the polymer. Compounds **29–31** were also coordinated to $Ru(bpy)_2$, and **29** and **30** to $Os(bpy)_2$. $Ru(bpy)_2$(**29**), $Os(bpy)_2$(**29**), and $Ru(bpy)_2$(**31**) were electropolymerized to form conducting films. The films showed only one metal-based oxidation in all cases.

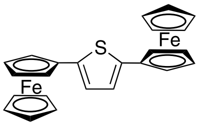


29 $R^1 = R^2 = H$
30 $R^1 = Me$, $R^2 = H$
31 $R^1 = Me$, $R^2 = OMe$

4.3. π-Complexes

4.3.1. Cyclopentadienyl

Ferrocenyl end groups are widely used in the study of metal–metal interactions over conjugated bridges. They are easy to synthesize, and are stable in both oxidized and reduced forms. For example, compounds **32** and **33** [34] were readily prepared from the $PdCl_2(PPh_3)_2$ catalyzed coupling of ferrocenylzinc chloride and the corresponding dibromothiophene. Both **32** and **33** showed coupling by CV, with $\Delta E = 150$ and 140 mV, respectively. Longer oligothiophenes (**34** and **35**) [35], have also been synthesized with the same procedure, using 5,5″-dibromo-3,3″-dihexylterthiophene or 5,5″-dibromo-3,3″,4‴,3⁗-tetrahexylsexithiophene in place of dibromothiophene. Although **34** and **35** show no electrochemical coupling, when oxidized with one equivalent of $FeCl_3$ a ligand-to-metal charge transfer (LMCT) band appears in the near IR region. Compounds incorporating vinyl and ethynyl groups (**36–43**) [36,37] have also been investigated. Diferrocenes **36** and **38** were synthesized by a Wittig reaction of ferrocenylmethylphosphonium bromide and the appropriate thienylaldehyde, **37** was synthesized by a McMurry coupling of the ferrocene-substituted thienylaldehyde in the presence of $TiCl_4$ and Zn, and **39–41** were synthesized by Sonogashira coupling of ethynylferrocene and the appropriate dibromothiophene. The $\pi \rightarrow \pi^*$ absorptions of these compounds were red-shifted with respect to the unsubstituted thiophene, indicating extended conjugation, but no electrochemical coupling was observed. Our group has also synthesized the 3,4-ethylenedioxythiophene derivatives **42** and **43**, also using Sonogashira coupling procedures [37]. No electrochemical coupling was observed, but when both Fe groups are electrochemically oxidized, a broad, low-energy band was observed in the near IR region (875–1290 nm), which was assigned as an oligothiophene → Fe(III) LMCT band. The intensity and position of the LMCT are related to the extent of delocalization in the compound, and it is clear that the intensity increases and energy decreases with an increase in conjugation length of the oligothiophene. Similar LMCT bands were also observed in **39–41**, as were the trends related to increases in oligothiophene length.



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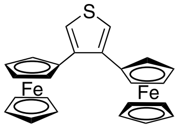

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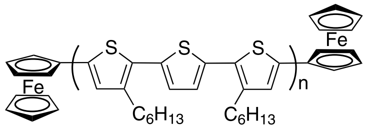
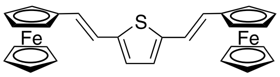


34 n=1
35 n=2



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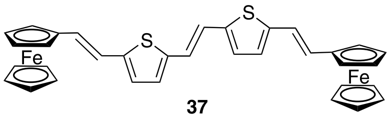

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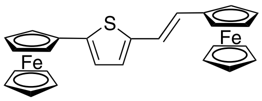

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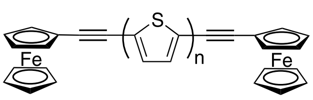
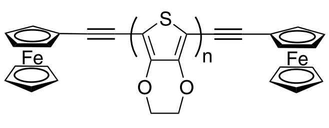
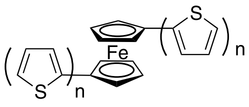


39 n=1
40 n=2
41 n=3

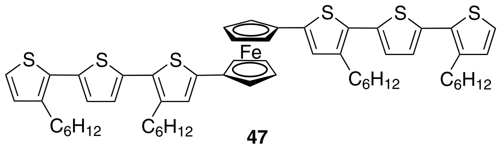


42 n=1
43 n=2

Polythiophenes can also incorporate ferrocenyl moieties, and several have been synthesized via electropolymerization of monomers. Our group has synthesized monomers of this type, for example, **44**–**46** [38,39]. Compounds **45** and **46** were synthesized via lithiation of **44** and coupling to 2-bromothiophene or 2-bromobithiophene in the presence of $ZnCl_2$ and $Pd(PPh_3)_4$. The UV–visible–near-IR spectra of the electrochemically-generated monocations contain oligothiophene → Fe(III) LMCT bands in all three compounds, as in **39**–**41**, and similar trends were observed. Compound **45** did not electropolymerize, while repeated scanning of **45** and **46** yielded conducting films on the electrode. The films were golden red at 0 V and became black when oxidized. Spectroelectrochemistry was performed on poly-**45** and poly-**46**, and an oligothiophene → Fe(III) LMCT band was observed at 1395 nm in poly-**45**. Again, the intensity of the transition increased and the energy decreased, with respect to **45**, as the conjugation length of the oligothiophene moiety increased from two to four units. In poly-**46** only a weak LMCT band is observed, possibly due to incomplete oxidation of the Fe groups. Higgins and co-workers have synthesized a soluble derivative of **46** by incorporating hexyl chains (**47**) [40]. Compound **47** was synthesized via Stille coupling of stannylferrocene and 5′-iodo-3,3″-dihexylterthiophene, and was electropolymerized to yield a conducting polymer film on the electrode. The oxidized film was blue while the reduced form was green and oligothiophene → Fe(III) LMCT bands were seen at 590 nm for poly-**47**.



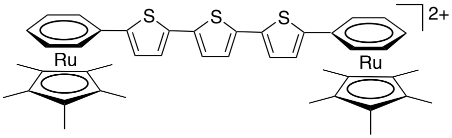
44 n=1
45 n=2
46 n=3



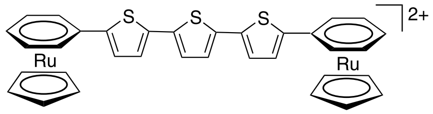
47

4.3.2. η^6-Benzene

Another π-type ligand that can easily be attached to an oligothiophene is benzene. Graf and co-workers [41,42] have synthesized **48**–**51** via Kumada coupling of bromobenzene and 5,5″-dibromoterthiophene, followed by reaction with the appropriate molar ratio of $[CpRu(CH_3CN)_3]^+$ or $[Cp^*Ru(CH_3CN)_3]^+$. The free ligand did not polymerize electrochemically and the oxidation potential changed very little from that of terthiophene, indicating poor conjugation of the terthiophene core with the phenyl groups. However, the UV–visible spectrum of the ligand shows a red-shift with respect to terthiophene, indicating some conjugation in the excited state. Upon complexation of the metal, the emission is red-shifted and the quantum yield of emission at 420 nm is reduced with respect to the free ligand, indicating internal energy transfer. Absorption is also slightly red-shifted in the complex, indicating excited state stabilization through an inductive effect of the metal. The oxidation potentials increase by about 150 mV per ruthenium group, due to an increase in positive charge, and a new, metal-based reduction process appears, but no electrochemical coupling was observed. Spectroelectrochemical studies were performed, but no IVCT band was observed.



48



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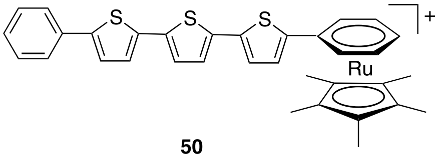

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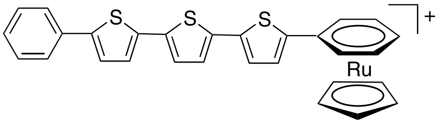

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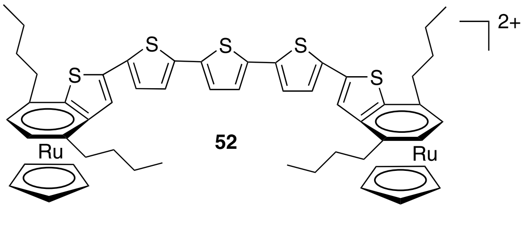


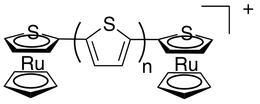
52

In fact, upon one- and two-electron oxidation the spectra of the complexes were very similar to those of other α-capped terthiophenes, suggesting that the positive charge is localized on the terthiophene core.

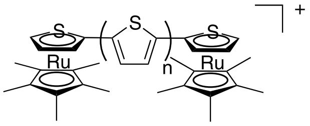
A benzene group has been fused directly to the thiophene core to create an inflexible ligating group via Kumada coupling of 2-bromo-4,7-di-*n*-butylbenzo[*b*]thiophene and 5,5″-dibromoterthiophene [43]. This compound was then complexed to $[CpRu(CH_3CN)_3]$ to yield **52**, which exhibits many of the same electronic and optical properties as the free ligand. Similar to **48**–**51**, a red-shift of the $\pi \rightarrow \pi^*$ band in the UV–visible absorption was observed, the strong emission band of the free ligand was quenched, the oxidation potentials were raised, and a metal-based reduction process appears in the CV. No electrochemical coupling was observed, and the spectroelectrochemistry was not investigated. Complex **52** is a rare example of an oligothiophene-bridged metal complex for which a crystal structure has been obtained.

4.3.3. *η⁵-Thiophene*

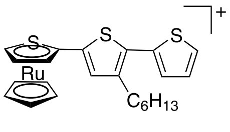
Similar to cyclopentadienyl, thiophene can coordinate in an η^5 manner to transition metal centers. For example, **53**–**56** were synthesized by reacting the appropriate oligothiophene with two equivalents of $[CpRu(CH_3CN)]^+$ or $[Cp^*Ru(CH_3CN)]^+$ ($Cp^* =$ pentamethylcylopentadiene) [41,44]. Upon electrochemical oxidation, all four complexes formed a conducting film on the electrode, but none showed evidence for metal–metal interaction by CV. In fact, binding a metal to one ring of the oligothiophene in a η^5-fashion effectively removed that ring from conjugation. This was also found in the investigation of **57**–**60**, [45] where blue shifts and loss of intensity in the $\pi \rightarrow \pi^*$ band occurred upon complexation. Compounds **57**–**60** were also synthesized by reacting the appropriate oligothiophene with $[CpRu(CH_3CN)]^+$. Complexes **57** and **60** were formed as a mixture of isomers; only the major isomer is shown.



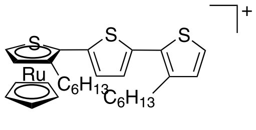
53 n=1
54 n=2



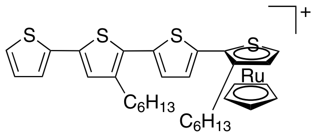
55 n=1
56 n=2



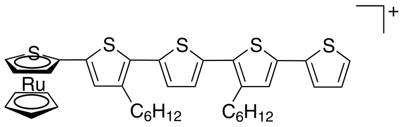
57



58



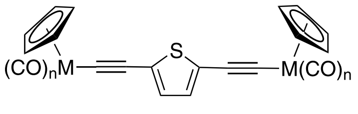
59



60

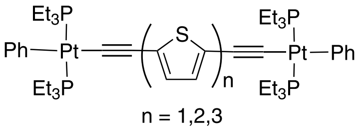
4.4. *Acetylene complexes*

Metal acetylide complexes can be synthesized via a number of coupling reactions. One route that has been successfully used is Pd(II) catalyzed cross-coupling of tributylstannylacetylene derivatives with metal halides to produce bimetallic complexes **61** [46]. No electronic properties of **61** were reported. Similarly, bis(platinum) complexes bridged with acetylide functionalized oligothiophenes were obtained by reaction of the bisacetylene ligands with an appropriate metal halide in the presence of CuI to give **62** [47]. No electrochemical data was reported for these complexes, but red-shifts were observed in the UV–visible spectra upon attachment of the Pt centers. Copper catalyzed coupling was also used to prepare Pt acetylide polymers **63** [48] in which evidence for enhanced delocalization was observed in the electronic spectra, which showed bathochromic shifts relative to dimers.



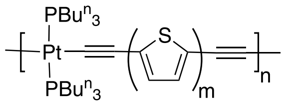
M = Mo, W, Fe, Ru; n = 2,3

61



n = 1,2,3

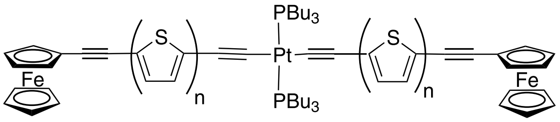
62



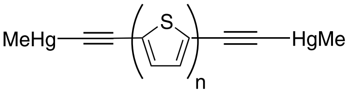
m = 1,2,3

63

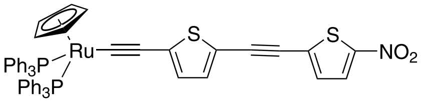
The Pt containing bis(ferrocenyl) acetylide complexes **64** show little interaction between the ferrocenes via electrochemistry, [49] but the presence of the Pt results in a bathochromic shift in the visible spectrum indicating enhanced conjugation, consistent with theoretical studies carried out by these authors. Recently, some interesting di(mercury) complexes (**65**) were reported, which also showed enhanced conjugation through a red-shift in the absorption spectrum [50]. The emission from these species is somewhat quenched by the presence of the metal. A series of Ru acetylide complexes have been prepared in which an organic acceptor group terminates the conjugated bridge; an example is **66** [51]. The linear and non-linear optical behavior of these complexes has been studied, and these workers found that the thiophene-containing bridges provided a more effective conjugated link between the metal donor and acceptor moieties than other aromatic linkers containing benzenes.



64 n = 1-3

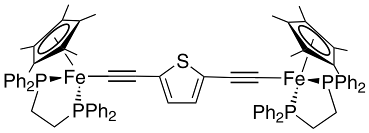


65 n = 1-3

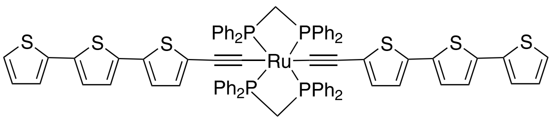


66

Lapinte and coworkers prepared the iron alkynyl complex **67** [52]. CV showed large interaction ($\Delta E = 340$ mV), and oxidation with ferrocenium allowed these authors to isolate the monocationic form of this complex. Near-IR and Mössbauer studies on the cation suggest that the odd electron is delocalized over the bridge on the timescale of these techniques, while on the fast infrared timescale, the two metal sites are inequivalent. Our group has prepared Ru acetylide polymers by electropolymerization of complex **68**, [53] and delocalization of charge onto the thiophene bridges was observed by electronic spectroscopy in these species.



67



68

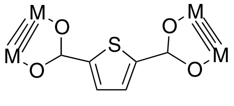
4.5. Oxo-linkers

Oxygen-containing groups have been used to coordinate oligothiophenes to two early transition metals, molybdenum and tungsten, with interesting result. Complexes **69** and **70** [54] were synthesized by complexing two equivalents of either Mo(CO$_2{}^t$Bu)$_4$ or W(CO$_2{}^t$Bu)$_4$ with 2,5-dicarboxythiophene. These are interesting as they incorporate metal–metal bonds into the conjugation pathway. Intense absorptions in the visible region arise from metal $\delta \rightarrow$ thiophene π^* transitions. Mixed valence complexes were prepared by oxidation with ferrocenium, and ESR experiments showed that the unpaired electron in **71** is delocalized over two metal centers, while **72** showed delocalization over four metals.

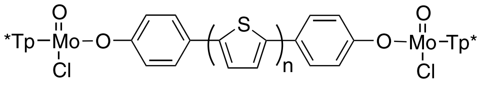
A series of bis-*p*-phenolate oligothiophene ligands were prepared via Stille coupling of stannyl thiophenes and 4-bromoanisole [17,55]. These were demethylated and complexed to a Mo capping group (**73–75**). The complexes showed strong metal–metal coupling by CV (ΔE values of 370, 250, and 170 mV, respectively). Upon electrochemical generation of the mixed valence species, intense and broad bands appeared in the near-IR region, characteristic in position and intensity of phenolate → Mo(VI) LMCT bands, which obscure the expected IVCT band. Compound **73** also exhibited weak antiferromagnetic coupling ($J = -3.6$ cm^{-1}). Two other ligands incorporating naphthyl in place of phenyl, **76** and **77**, [56] were also synthesized. Compound **77** was synthesized using 1-methoxy-4-iodonaphthalene, while **76** was synthesized with step-wise Negishi coupling of 2-thienyl zinc(II) bromide and 1-methoxy-4-iodonaphthalene catalyzed by [PdCl$_2$(PPh$_3$)$_2$], followed by lithiation, reaction with zinc(II) bromide, and a second Negishi reaction with 4-iodoanisole. Both **76** and **77** were then complexed to Mo. Interestingly, the addition of the large napthyl groups reduces ΔE to 250 and 140 mV, respectively, presumably because their steric bulk decreases conjugation in the ligand. Intense LMCT bands in the near-IR region obscure the expected IVCT bands in these compounds as well.

4.6. Salen based

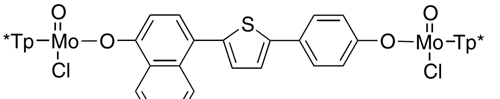
Two groups have investigated polymers prepared by electropolymerization of salen-based monomers containing thio-



69 M=Mo(O_2C^tBu)$_3$
70 M=W(O_2C^tBu)$_3$

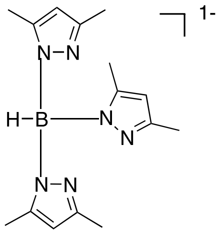


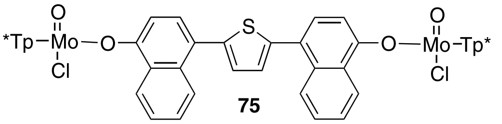
71 n=1
72 n=2
73 n=3



74

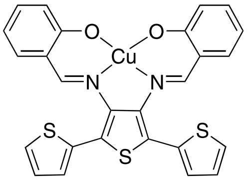
Tp* =



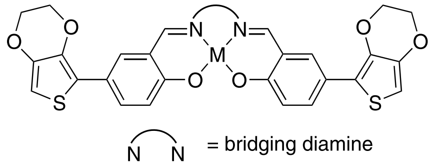


75

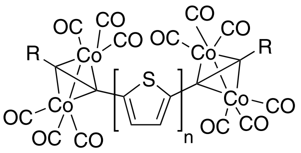
phenes (**76** and **77**) [57–60]. These systems form interesting materials, in which metal redox waves are observed in some cases; however, no direct metal–metal interaction is observed. The conductivity of polymers formed from **77** with different metals in the backbone show differing degrees of dependence on the interchain spacing, which is controlled by varying the bridging diamine.



76

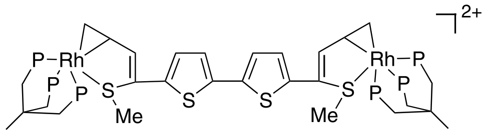


77 M = Co, Cu, Ni, UO_2



78

n = 1-3
R = *n*-butyl, phenyl



79

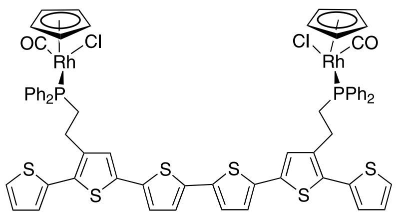
4.7. Miscellaneous

In addition to the bonding modes and ligands described in the sections above, several other types of attachments have been prepared—although often only one example is known. These are collected in this section.

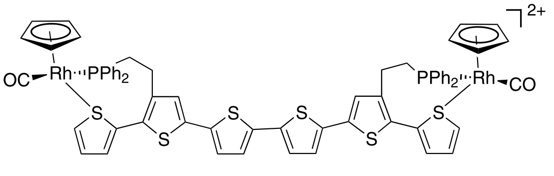
Shin and coworkers have prepared a series of Co derivatives **78** by reaction of $Co_2(CO)_8$ with α,ω-bis(alkynyl)oligothiophenes of different lengths [61]. These have been examined by CV and show oligothiophene-based oxidation waves as well as a single irreversible reduction wave due to the metal clusters. The absence of electronic interactions between the metal groups in these complexes is attributed to the irreversibility of the reduction process. An interesting ring-opening reaction with a Rh hydride complex has resulted in the preparation of the bimetallic complex **79** [62] in which the two terminal thiophene rings have been opened. No electronic properties of this complex have been reported yet.

Mirkin and coworkers have isolated a dimetallic Rh complex **80** in which the two metal centers are electronically isolated from the conjugated backbone via an ethylene group and no interaction is observed via CV [63] however, this work is noteworthy as the sexithiophene complex was structurally characterized in the solid-state. Dechlorination of **80** provides the thiophene coordinated complex **81**, but the metal redox waves are inaccessible in CH_2Cl_2, and thus interaction could not be probed electrochemically.

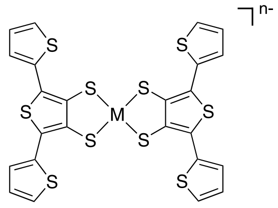
Skabara has electropolymerized bis[(terthiophene)dithiolene] complexes (**82**) containing Ni(II), Pd(II) and Au(III) [64]. These films show only one redox wave for the metal dithiolene unit, which is less reversible than in the monomer,



80



81



82

M = Ni(II), n = 2; Pd(II), n = 2; Au(III), n = 1

suggesting there is little interaction between adjacent metal units in the film.

5. Summary and future directions

The studies summarized in this review demonstrate that significant effort has been directed towards the synthesis of complexes in which terminal metal groups are used to probe interactions across a variety of thiophene-containing bridging groups. The ability to prepare pure complexes, and to characterize them fully, has resulted in the development of a framework of understanding of the electronic interactions between metal complexes and conjugated bridges.

Almost all of the complexes which have been prepared with thiophene-containing bridges show evidence of the electronic influence of the metal groups. The most common manifestation of this are red-shifts in the $\pi \rightarrow \pi^*$ transition on the conjugated bridge or in charge transfer bands involving the metal and orbitals on the bridge. These shifts, however, do not conclusively demonstrate electronic interactions between terminal metal groups. Strong evidence for this is provided by electrochemical interactions (ΔE). Of the complexes surveyed the largest ΔE values were observed in cases where the metal is bonded directly to the end of the conjugated bridge, via a nitrogen (Mo complex of **6**–**8**), an oxygen (**72**–**74**), or a carbon (**68**). The interaction is strongest for shorter bridges, and generally drops off as the number of thiophene units increases, however, complex **74** is notable as it has a ΔE of 170 mV with a five-ring bridging ligand! It would be of significant interest if these impressive results could be obtained in longer polymer systems with multiple metal centers interacting over similar distances. Many complexes of Ru have been studied, however, virtually none of these show any electrochemical interaction, although some do show spectroscopic evidence for intermetallic interaction. This is likely a consequence of the mismatch in energy between the high lying HOMO of many ruthenium bipyridyl and terpyridyl complexes with orbitals on the bridge which can participate in allowing interaction between the metal groups [65]. Ruthenium complexes in which the HOMO better matches energetically an orbital on the bridging ligand, such as cyclometallated bipyridyl derivatives (for example **21**) may show larger interactions and are worth investigating.

Linkages involving π-complexes (ferrocenes, η^6-benzene, η^5-thiophene etc.) generally do not lead to strong interactions. Only the diferrocenyl complex **32** and **33**, in which the bridge is short, showed a slight electrochemical interaction. In these types of complexes, the conjugation between the π-complexing ring and the remainder of the bridge may be poor, as has been suggested for complexes such as **48**–**51** where the benzene is poorly conjugated to the thiophene in the ground state.

At this stage, our understanding of longer oligomeric or polymeric systems containing metals is still rather primitive. Although some of the experimental techniques that have been utilized for the small complexes have been extended to longer systems, complications due to the lack of well-defined structure make interpretation of these experiments more challenging. In the future what will be needed are a greater range of polymeric systems incorporating some of the same metal groups, which have been examined in the model complexes. It would be of interest to apply coupling methodologies such as those used by Tour [66] for the construction of monodisperse, conjugated phenyleneethynylene oligomers, to metal-containing systems. This would provide a series of oligomers of varying lengths, the properties of which could be studied in a systematic fashion.

It would also be interesting to see future efforts devoted to preparing complexes similar to the dithienylethene bridged **21**. Incorporating optically or chemically switchable groups into the bridge will be of interest in possible future applications of these materials in nanoscale devices. In conclusion, research in this field to date has focused on the synthesis and characterization of a number of relevant and interesting complexes and materials. Within this framework, it is hoped that future work will flesh this work out with more compounds using these and new linker groups to connect the metal and conjugated backbone; and that further in depth exploration of the electronic behavior will be carried out.

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