



Review

Electropolymerisable dithiolene complexes

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Contents

1. Introduction	1549
2. Ligand synthesis	1550
2.1. Synthesis via the α -halo carbonyl	1550
2.2. Synthesis via the alkyne	1551
2.3. Other synthetic routes	1551
3. Complex synthesis	1551
3.1. Symmetrical dithiolenes	1551
3.2. Mixed ligand dithiolenes	1551
4. Monomer structure and properties	1553
4.1. Symmetrical dithiolenes	1553
4.2. Mixed ligand dithiolenes	1553
4.3. Fused dithiolenes	1554
5. Polymerisation	1554
6. Polymer properties	1555
6.1. Redox properties	1555
6.2. Optical properties	1556
6.3. Conductive properties	1557
6.4. Switching behaviour	1557
7. Summary and future outlook	1557
Acknowledgements	1558
References	1558

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ABSTRACT

The emerging field of polymerisable metal dithiolenes, where one or more of the ligands is capable of covalently linking to another, is discussed and the physical and electronic properties of the molecular and polymeric materials compared. Materials that display both the interesting redox and optical properties of metal dithiolenes, whilst possessing the enhanced stability and electronic communication of an organic polymer framework, would find widespread application in many areas of materials science. The rational design of such materials is therefore of key importance in the production of new dithiolene containing functional materials for the development of novel multi-functional devices. Although the field is currently small, many interesting observations have already been made that allowed us to relate aspects of structure to function. In particular, the redox and optical properties appear to be strongly dependent on the linking positions within the polymer, imposed by the ligand design, and able to be tuned through strategies such as copolymerisation.

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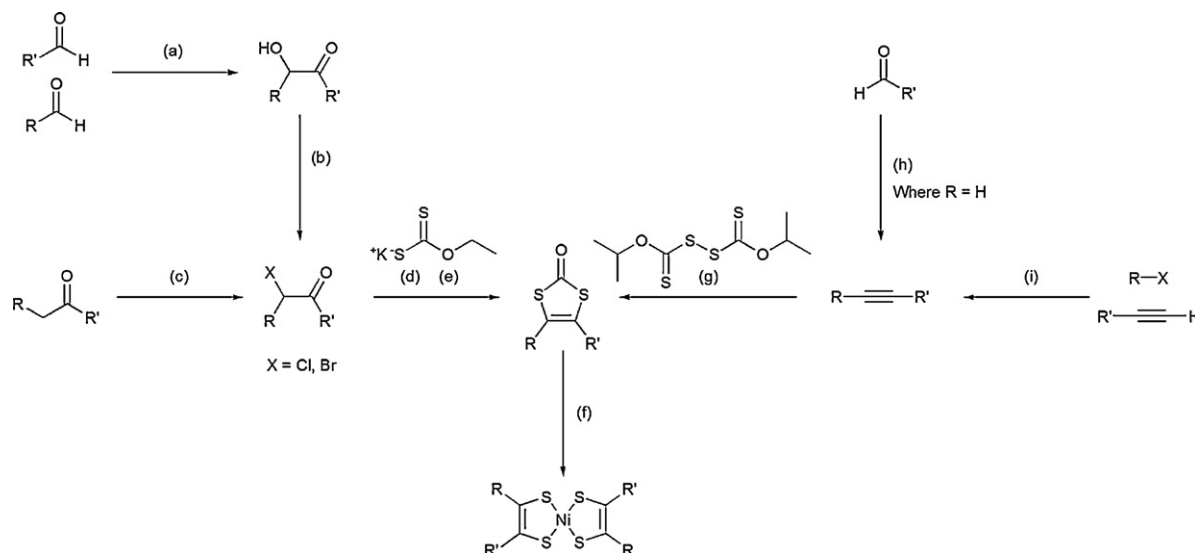
1. Introduction

Since the seminal work of Schrauzer and Mayweg in the early 1960s [1], metal dithiolenes [2] have found widespread application

within the field of materials chemistry. Their magnetic properties have been investigated and shown to yield ferromagnets, ferrimagnets, metamagnets and spin ladders. Such systems have provided the field with great insight into the study of magnetic ordering [3]. Their conductive properties have been tuned to develop semiconductors [4], molecular metals and superconductors [3,5] due to their multiple stable redox states and, often, highly planar molecular geometry (especially for d^8 systems), allowing for effi-

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Scheme 1. Suitable synthetic routes to symmetric polymerisable nickel dithiolenes from commercially available starting materials. (a) 3-Benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride (cat.), NEt₃, EtOH, Δ; (b) PPh₃, CCl₄/DCM; (c) CuBr₂, EtOAc, Δ; (d) KS(CS)OEt, acetone; (e) HBr/AcOH; (f) [TMA][OH], NiCl₂·6H₂O, MeOH, THF; (g) diisopropyl xanthogen disulfide, AIBN, benzene, Δ; (h) (Ph₃P⁺CH₂Br)[−], ^tBuOK, THF, −78 °C; (i) Pd(PPh₃)₂Cl₂, CuI, NEt₃, DMF.

cient intermolecular electronic communication. As a result of their intense NIR absorption and high thermal and photochemical stability [6], their optical properties have been harnessed for Q-switching near-infrared (NIR) lasers [6,7] and their development as non-linear optic (NLO) chromophores [8]. Long excited state lifetimes and highly tuneable absorption profiles also offer the possibility for their incorporation into photovoltaic devices [9]. In recent years, a great deal of interest has been focussed on the development of multi-functional metal dithiolenes [10]. Beyond their being of academic interest, an interplay between their optical, magnetic and conductive properties might lead to the development of optoelectronic or magnetooptic materials for novel device construction.

Over the past 40 years, many reviews have looked at different aspects of dithiolenes functionality, and this special issue of *Coordination Chemistry Reviews* is a testament to the fact that the field is still growing. In the last decade, a few groups have become interested in developing methods of stabilising the functionality of the dithiolenes in a conjugated organic polymer framework [11–13]. Incorporation into such a conjugated system offers the possibility of materials that combine the properties of the polymer, such as conductivity, flexibility and good stability [14], with the magnetic, redox and optical properties of the dithiolenes [12]. Such materials could then be deposited directly onto flexible substrates by electrochemical or solution methods to form flexible devices, such as organic light emitting diodes and photovoltaics [15]. This review is focussed on the nascent field of polymerisable metal dithiolenes and, by identifying the drive behind our work and that of others, as well as looking at the results already obtained, we hope to relate properties of structure to function to allow a more targeted approach to complex design. By collating the results already obtained, we may also look to the not too distant future and to what this field may yet yield.

Previous reviews on dithiolenes have focussed, without exception, on the molecular and bulk properties of dithiolenes monomers. These reviews fall into two groups: general overviews of dithiolenes chemistry, which continue to be produced in an effort to collate the continuing and numerous contributions from a great many groups [2,16], and those that focus on specific aspects of dithiolenes chemistry, such as their magnetic [3], conductive [17], optical behaviour [6,18] or biological relevance [19]. This list is by no means exhaustive, but serves as a good starting point for a more in-depth

understanding of these fascinating systems. In this review, we will look at the general features of the dithiolenes monomers possessing polymerisation potential only for comparison with the resultant polymeric materials. For a more detailed discussion of the general properties of dithiolenes monomers, the reader is directed to the above reviews and references therein.

2. Ligand synthesis

A great deal of work has been devoted to developing stable metal dithiolenes ligand precursors, and this is reflected in the plethora of literature devoted to dithiolenes ligand design, addressing the various synthetic constraints imposed by the desired functionality of the ligand [19]. The synthesis of polymerisable dithiolenes possesses its own constraints as the synthesis of such systems is complicated by the reactivity of the polymerisation terminals, and thus often requires the use of less-aggressive techniques to effect the desired transformation.

Two key synthetic routes have been developed that are suitable for the general preparation of polymerisable dithiolenes ligand precursors; either via an α-halo carbonyl and subsequent reaction with a xanthate ester salt, or via an alkyne and subsequent free radical reaction with xanthogen disulfide (Scheme 1). Both routes yield a 1,3-dithiol-2-one which can readily and stoichiometrically be deprotected to form a 1,2-dithiolate salt *in situ* for reaction with an appropriate metal salt. The resultant complexes can then be oxidised under mild conditions to afford the neutral species.

2.1. Synthesis via the α-halo carbonyl

Charlton et al. described the synthesis of two 4,5-dithiophen-yl[1,3]dithiol-2-ones, the 2-thienyl [20,21] and 3-thienyl [13], via a benzoin condensation reaction of the appropriate starting thiophene carboxaldehyde. The α-hydroxy ketones could then be converted in high yield under mild conditions to the α-chloride by reaction with CCl₄ and PPh₃. Reaction with potassium ethyl xanthate, followed by acid mediated ring closure yielded the target dithiol-2-ones in 30–50% overall yield. Though this method is useful for symmetrically substituted pendent dithiolenes, the reaction is complicated and in some cases fails completely for cross-condensation or for systems that are particularly electron

deficient. This is due to the fact that the benzoin reaction relies on a delicate balance of proton donor and acceptor ability of the aldehydes. Where the reaction does fail, α -halogenation of a ketone can afford the desired α -haloketone in similarly high yields [22]. Care should be taken for such a transformation as halogenation using bromine or NBS could result in premature polymerisation of the ligand [23]. Bromination can be achieved in such sensitive systems by using CuBr_2 [22] and the resultant α -bromide can then be converted in similar yields to the desired dithiol-2-one as suggested above.

2.2. Synthesis via the alkyne

A perhaps more versatile route to dithiol-2-ones was devised by Gareau and Beauchemin [24]. They showed that alkynes could be readily converted to the target dithiol-2-one by reaction with diisopropyl xanthogen disulfide using AIBN as a radical initiator. The usefulness of this route originates from the wide availability of alkynes due to the versatility of the Sonogashira (and other) coupling reactions. High yielding alkyne-forming reactions can, and have, been designed for a huge number of commercially available aryl halides. In our experience, for less electron rich aryl halides, improved yields are best achieved by use of aryl iodides [25,26], or by the use of Stille methods [27] rather than harsher reaction conditions, such as high temperature or microwave irradiation, as such conditions tend to promote unfavourable side reactions at the polymerisation terminals, though the nature of the by-products was not fully established [26].

Kean et al. showed such a route to be suitable for both symmetric and unsymmetrically thienyl substituted bis-aryl alkynes (**1** and **3**) and, more recently, we showed the route to be suitable for mixed alkyl-aryl indole substituted alkynes (**4**) (Fig. 1) [26].

Although reductions in yield are observed, the originative work by Gareau et al. showed the reaction to proceed even for very bulky substituents, thus this quick method remains a powerful general route into 1,3-dithiole-2-ones.

2.3. Other synthetic routes

The two routes described above represent perhaps the most versatile and efficient general routes toward a stable dithiolene ligand precursor. Other routes have also been developed that are suitable for the synthesis of specific polymerisable dithiolene ligand precursors.

Work by Skabara et al. [12] achieved a dithiol-2-one with pendent thiophene groups by coupling thiophene carboxaldehydes directly to a vinylene trithiocarbonate. This elegant route afforded the dithiolene fused to a thiophene backbone (**5**). The effect of this structural constraint will be discussed in detail later; however, the fused backbone is an intrinsic outcome of this route.

Conversion of an α -dione directly into a stable dithione using P_4S_{10} or Lawesson's Reagent is a quick and mild route to dithiolene ligands [28], however, this is only possible in heavily resonance stabilised and structurally constrained systems, and thus is only suitable in a limited number of cases. Related to this, direct reaction of an α -hydroxy ketone with P_4S_{10} [29,30] remains a useful, quick and relatively mild route to metal dithiolenes, however, the yields obtained are often poor due to the lack of stoichiometric control over the subsequent metal coupling.

3. Complex synthesis

The synthesis of metal dithiolenes from dithiol-2-ones has been well documented in the literature; however, certain restraints are put on the synthesis and isolation of the target complexes, imposed

by the sensitivity of the ligand. Symmetric and mixed ligand dithiolenes will be looked at separately as the problems encountered for each system are distinct (Fig. 1).

3.1. Symmetrical dithiolenes

From a substituted dithiol-2-one ligand precursor, the desired symmetric metal dithiolene is readily afforded by a stoichiometric reaction with a base, such as $[\text{TBA}][\text{OH}]$ or NaOMe , followed by the addition of the appropriate metal salt, and tetralkylammonium salt where an anion is to be isolated (Scheme 1). The dianion may be observed in some cases, but is readily oxidised in air to the monoanion or the neutral species. For polymerisation, the neutral species are preferable to avoid the complication of deposition of the neutral monomer on the electrode [31]. For more conventional dithiolene systems, oxidation of the dithiolene anion is most commonly achieved with elemental iodine [13,31], however, for more sensitive systems, less aggressive methods have been employed. Anjos et al. achieved oxidation of $[\mathbf{8}][\text{TMA}]$ by leaving an acetone solution of the TMA salt open to atmospheric oxidation [13]. Dalgleish and Robertson afforded **12** by passing a DCM solution of the $[\mathbf{8}][\text{TMA}]$ salt over a silica plug [26].

In general, the reduced solubility of the neutral species in polar solvents, compared to the anion is a useful tool for affording pure, crystalline samples of a neutral symmetric metal dithiolene.

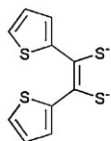
3.2. Mixed ligand dithiolenes

The synthesis of mixed ligand nickel dithiolenes encounters its own complications due to the observed lability of the dithiolene ligand. This can be used to our advantage in the synthesis of such complexes [32,33], but can often work against us and lead to mixed products, especially for more electronically similar mixed ligand dithiolenes. By mixing equimolar amounts of symmetrical dianionic and dicationic *bis*-dithiolene salts, Bigoli et al. showed almost quantitative conversion to the mixed ligand nickel dithiolene in a number of cases [34]. This route is highly ligand dependent and works best when the mixed ligand target is distinctly $\text{M}[\text{dithione}][\text{dithiolate}]$ in character. Such lability is more typical for nickel dithiolenes. Under identical conditions, both palladium and platinum dithiolenes more commonly precipitate as a charge transfer salt of the symmetrical metal dithiolenes, although mixed ligand complexes have recently been prepared [35]. This presumably reflects the improved orbital overlap of a larger metal with the diffuse sulfur orbitals. For more electronically similar mixed ligand and nickel dithiolene complexes, statistical product mixtures are common, with the desired product isolatable, in many cases in poor yield, by successive recrystallisation or column chromatography [36].

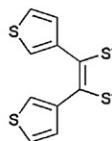
An alternative route is achieved by stoichiometric reaction of free ligand with a mono-dithiolene and has been shown by various groups to yield sufficient quantities of the mixed ligand product. Chen et al. demonstrated this method by the reaction of a stable α -dithione with $\text{Ni}(\text{mnt})_2(\text{NH}_3)_2$ in solution [32] and Dalgleish et al. showed a sodium dithiolate salt to react with $\text{Ni}(\text{R}_2\text{pipdt})\text{Cl}_2$, generated *in situ*, with the desired product (**14a** and **14b**) isolatable by column chromatography [37].

Due to the ligand lability observed in mixed ligand nickel dithiolenes, the high lattice strength of a charge transfer complex of the symmetric dithiolenes may drive the equilibrium away from the target mixed ligand complex, thus it is important to observe the solution behaviour of such a complex over time as their long term stability is of paramount importance if such complexes are to be useful in devices.

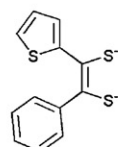
Symmetrically Substituted Dithiolene Ligands



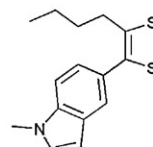
bis-(2-thienyl)-1,2-ethylenedithiolate
(b-2ted)
1



bis-(3-thienyl)-1,2-ethylenedithiolate
(b-3ted)
2

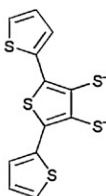


1-Phenyl-2-(2-thienyl)-1,2-ethylenedithiolate
(p-2ted)
3

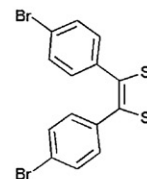


1-(N-methylindol-5-yl)-hex-1-ene-1,2-dithiolate
(mi-5hdt)
4

Fused-backbone Dithiolene Ligands



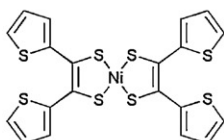
4,6-bis-(2-thienyl)-thieno-[3,4-c]-1,3-dithiolate
(b-2tted)
5



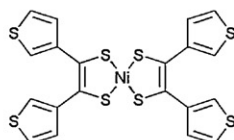
1,2-bis-(4-bromo-phenyl)-ethene-1,2-dithiolate
(b-4bped)
6

Ligands for Cathodic Polymerisation

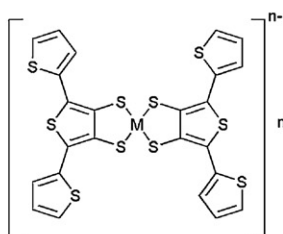
Symmetric Metal Dithiolenes



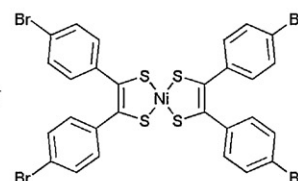
[Ni(b-2ted)₂]
7



[Ni(b-3ted)₂]
8

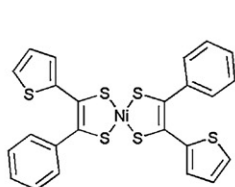


9a: [Ni(b-2tted)₂][TBA]₂
9b: [Pd(b-2tted)₂][TEA]₂
9c: [Au(b-2tted)₂][TBA]

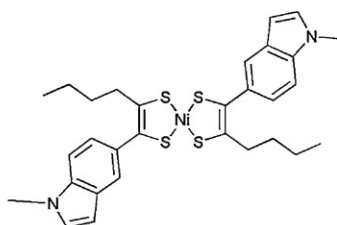


[Ni(b-4bped)₂]
10

Unsymmetrically Substituted Metal Dithiolenes

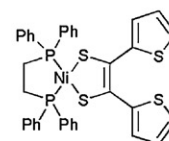


[Ni(p-2ted)₂]
11

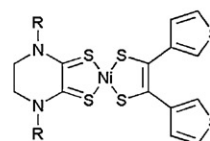


[Ni(mi-5hdt)₂]
12

Mixed Ligand Metal Dithiolenes



[Ni(dppe)(b-2ted)]
13

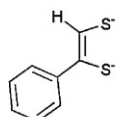


[Ni(R₂pipd)(b-3ted)]
14a: R=Bz
14b: R=Pr

Other Model Dithiolene Ligands

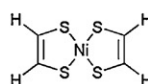


Ethene-1,2-dithiolate
(ed)
15

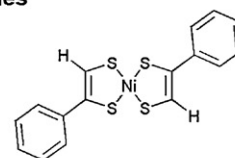


1-Phenyl-ethene-1,2-dithiolate
(ped)
16

Other Model Metal Dithiolenes



[Ni(ed)₂]
17



[Ni(ped)₂]
18

Fig. 1. Structure and naming guide for known metal dithiolenes discussed in this review. N.B. The structure of unsymmetrically substituted metal dithiolenes is shown in their trans geometry (vide infra).

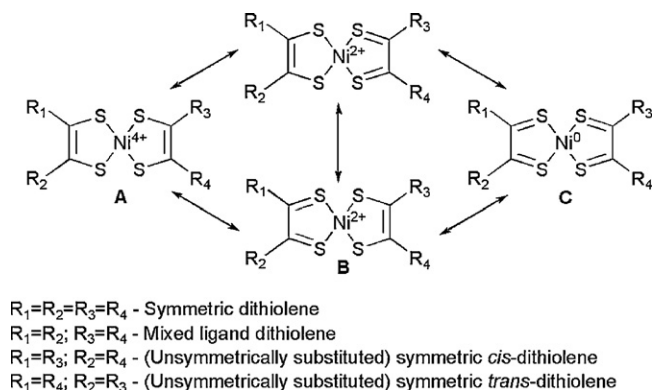


Fig. 2. Resonance forms of neutral nickel dithiolenes.

4. Monomer structure and properties

Many reviews have looked at dithiolene structure in general terms and some have investigated its effect on specific properties. We will discuss dithiolene monomer structure specifically related to polymerisable systems (though some non-polymerisable examples are included for comparison) in the hope of relating certain key structural features to the observed properties of the resultant polymers. The materials in question fall into three distinct structural classes: symmetrical dithiolenes, mixed ligand dithiolenes and fused dithiolenes, and they will each be discussed separately (Fig. 2). For the purposes of this review, we have grouped systems where the ligand is unsymmetrically substituted (herein referred to as unsymmetrically substituted dithiolenes) with the symmetrical dithiolenes due to their broadly similar behaviour upon polymerisation. Where the ligands are different on either side of the complex, we shall refer to these as mixed ligand dithiolenes.

4.1. Symmetrical dithiolenes

Symmetric *bis*-dithiolenes, where the ligand system is the same on both sides of the complex, are best thought of as a resonance hybrid of the limiting forms **A** and **C** (Fig. 2). Formal oxidation state of the metal thus becomes ambiguous and such complexes are best characterised in terms of their electronic structure. Dithiolenes are examples of non-innocent ligands and possess their own rich redox behaviour. The nature of the R groups therefore plays a key role in the electronic structure of the resulting complexes. In polymerisable systems, at least one of the R groups is capable of covalently linking to another and is typically a simple heterocycle, such as thiophene or indole and will therefore yield a mild inductive effect due to resonance stabilisation. The effect of this is a bathochromic shift in the NIR absorption profile due to a raising of the HOMO orbital compared to the unsubstituted ethane dithiolate (**17**) [16].

For systems where both ligand R groups are heterocyclic, there exists a large steric constraint on the ligand. This is shown in the X-ray crystal structures by the out-of-plane twist of the pendent groups [13,38]. This twist imparts a large effect on the redox properties of the complex and may help to improve reversibility of the oxidation of the dithiolene core to the monocationic species. For systems where this steric constraint is reduced, or removed altogether, better electronic communication between the dithiolene core and the polymerisable ligands is achieved by the free rotation of the ligand and the reversibility of the dithiolene oxidation is reduced [11] or removed entirely [26] as the radical cation can be easily delocalised to the periphery. Accordingly, for systems discussed below, this oxidation can then result in polymerisation of the peripheral heterocycles [11,26].

Interestingly, even in systems where such steric constraints are removed such as **18**, the complexes are shown to crystallise with the aromatic group twisted out of the molecular plane by a minimum of $\sim 25^\circ$ [39,40]. This has previously been attributed to lattice constraints or ignored altogether, however, geometry optimised structures of single molecules in the gas phase have also been shown to display such a twist [26,41]. To investigate this effect further, studies were carried out [41] using the same level of theory as had previously shown good structural approximation for nickel dithiolenes [37]. The results showed that a node exists in the HOMO orbital between the dithiolene core and the pendent aromatic group(s) on the linking C–C bond. Planarity of the structure is thus disfavoured by a repulsive electronic interaction between out-of-phase π systems, similar to the case observed in biphenyl systems [42,43]. However, the pendent aromatic does not align perpendicular, but lies twisted by ~ 20 – 30° away from coplanarity (Fig. 3a). This is thought to be due to a secondary conjugative interaction between the rings, which is maximised in the twisted conformation.

Fig. 3b shows a representation of the phase of the molecular orbital on the two ring systems. When the rings are perpendicular, there is an equal and opposite interaction between the rings, however, in the twisted conformation, the favourable interaction is maximised. This can be seen in the expanded isosurface plot of the HOMO of **15** (Fig. 3d).

Though the barrier to rotation is relatively small at ~ 5 – 15 kJ mol^{-1} (similar to that of butane rotation), it seems to be sufficient to affect the packing structure of smaller pendent aromatic groups in the crystal lattice (Fig. 3a) [26,40]. This twist may have an effect on the resultant film morphology by affecting molecular packing or promoting cross-linking of polymer chains.

For systems where the ligands are substituted unsymmetrically, there remains a question over their absolute conformation. The majority of nickel dithiolenes with unsymmetrically substituted ligands have been shown to crystallise in the *trans* conformation, though some examples of the *cis* conformation, especially where the steric difference is small, have been reported [44,45]. This is most likely due to the increased stability of the centrosymmetric geometry in the crystal lattice. However, recent literature has suggested that this may not be the case in solution [40,46]. Studies of the solution conformation of unsymmetrically substituted nickel dithiolenes by variable temperature NMR showed a coalescence of signals, separating into two distinct peaks at low temperature [40,46]. This suggests that such complexes exist in two isomeric forms, *cis* and *trans* and that they are rapidly interconverted at room temperature. Jeannin et al. went on to estimate the free energy of activation for this process [46]. From such a study it would be possible to assess the likelihood of different mechanisms of isomerisation. The barrier to inversion via a tetrahedral intermediate has been calculated to be more than twice that observed by NMR and thus it is likely that the process goes by another route, possibly linked to the lability of the ligand observed for nickel dithiolenes [34]. As polymerisation is a solution based process, the effects of such an isomerisation may be significant but have not yet undergone detailed study.

4.2. Mixed ligand dithiolenes

Some mixed ligand dithiolenes have been shown to possess interesting optical properties, in particular the class of mixed ligand *bis*-dithiolenes with two dissimilar dithiolene ligands, many of which are discussed by Deplano and Pilià in more detail elsewhere in this special issue [47]. In those examples, these properties arise from the differing contribution of each ligand to the frontier molecular orbitals. This results in the HOMO and LUMO orbitals becoming localised on different ligands, resulting in the lowest energy tran-

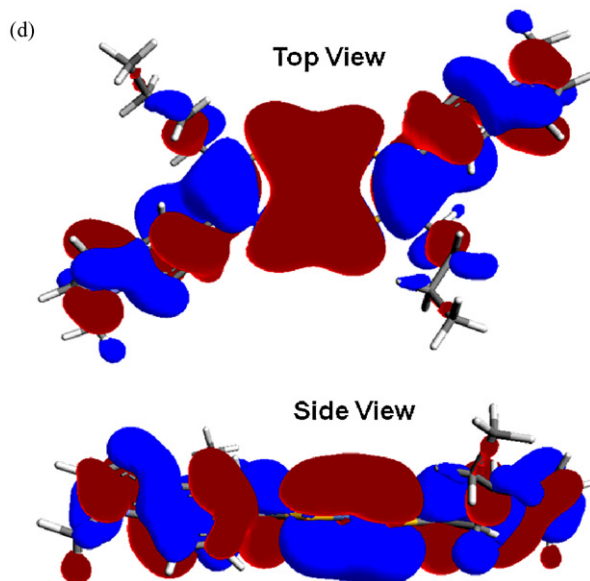
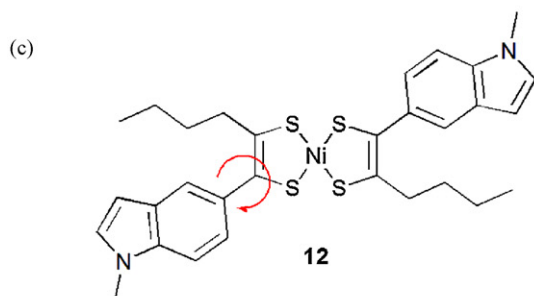
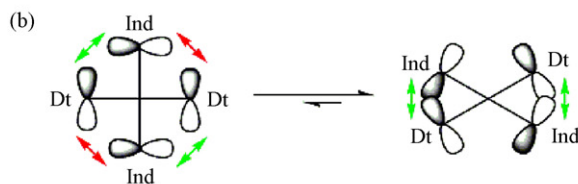
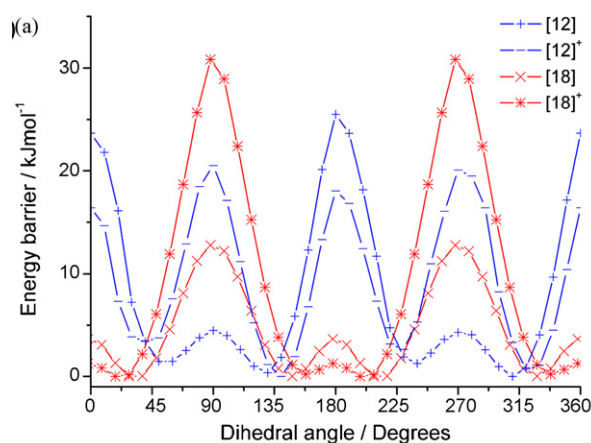


Fig. 3. (a) DFT calculated torsional potential surfaces for **12** and **18** in their neutral and oxidised state (B3PW91/6-31G*); (b) the pictorial representation of the HOMO density on the adjoining dithiolene (Dt) and indole (Ind) rings, showing favourable and unfavourable interactions in a perpendicular and twisted conformation; (c) pictorial representation of the investigated ligand rotation of **12**; (d) the HOMO of **12** (isosurface value is 0.01 e/Å³) [26,41].

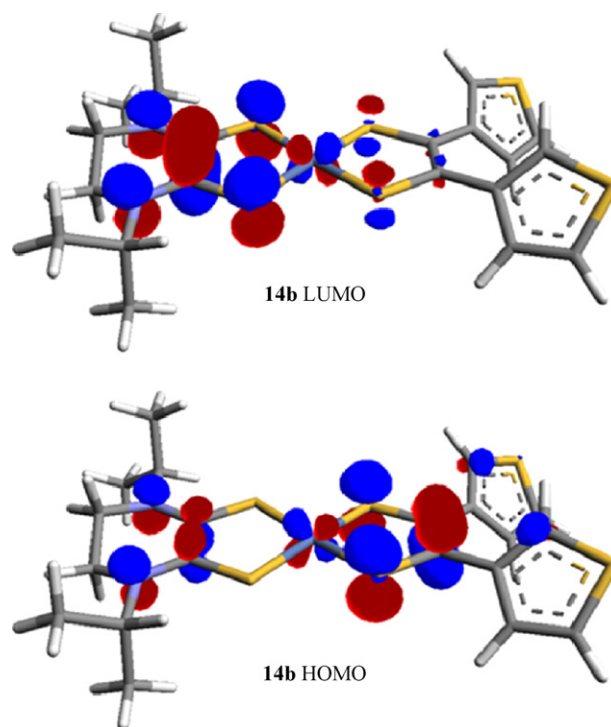


Fig. 4. DFT calculated frontier molecular orbitals of **14b** (B3PW91/6-31G*) [37]. Reproduced by permission of The Royal Society of Chemistry.

sition becoming inter-ligand charge transfer in character (Fig. 4). Such complexes are currently under intensive investigation as second order non-linear optic chromophores [8].

Mixed ligand dithiolenes are also desirable candidates for polymerisation due to the potential for fine tuning of the properties of the resultant film. Previous studies on mixed ligand dithiolenes have shown the solid state, redox and optical properties of the monomer to be tuneable by simple changes in the supporting ligand [33,37], and thus such systems offer exciting potential for the development of polymer systems that require precise redox or optical properties.

4.3. Fused dithiolenes

The effect of fusing an aromatic group directly to the dithiolene results in markedly different properties compared to the pendent systems previously discussed. A number of dithiolenes containing fused thiophene units have been prepared and studied in crystalline salts and a thorough review of such molecular systems is discussed elsewhere [48] and in this special issue by Belo and Almeida [49]. Although some of these may be interesting candidates for future work on electropolymerisation, in this review we restrict our attention to examples where such studies have already been reported.

5. Polymerisation

Coupling by oxidative electropolymerisation [50–52] is, by far, the most studied route to polymeric materials based on metal dithiolenes. Though such a technique is suitable for many niche applications, especially where the redox behaviour of the material needs to be controlled [53,54], for larger scale applications, such materials need to be synthesised and processed in bulk by chemical means. The inherent complications of chemical polymerisation, such as harsh conditions and difficult purifications, as well as the poor solubility of the resultant polymers, represent a substantial future challenge in the field, and one that will need to be addressed

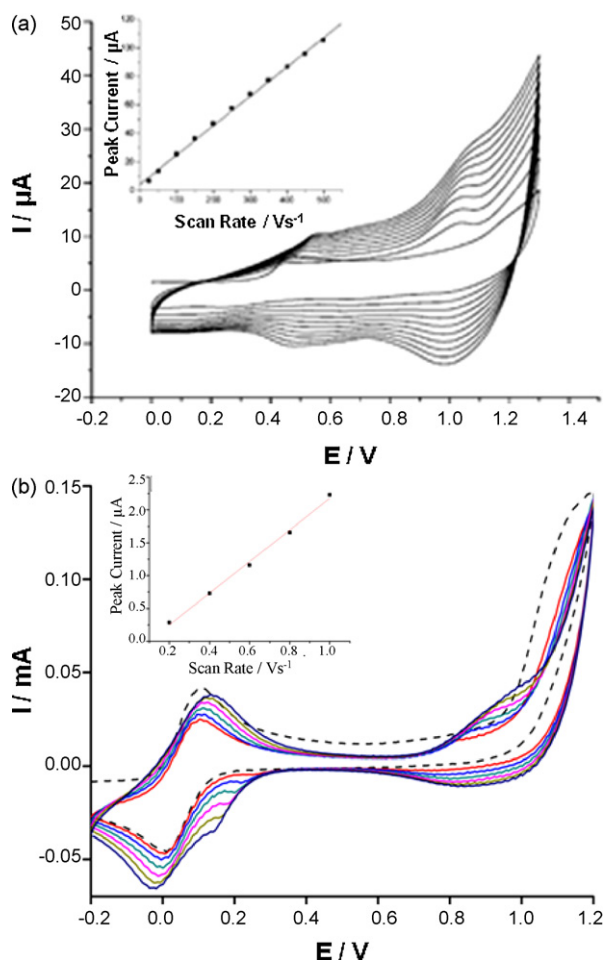


Fig. 5. (a) Polymerisation of **9a** on a glassy carbon working electrode using Ag/AgCl reference and platinum counter electrodes (DCM/[TBA][PF₆]). Insert: plot of scan rate vs. peak current for reversible redox process of a poly-**9a** coated glassy carbon electrode in monomer free electrolyte solution (MeCN/[TBA][PF₆]) [12]. Reproduced by permission of The Royal Society of Chemistry; (b) polymerisation of **12** on a platinum working electrode using Ag/AgCl reference and platinum counter electrodes (MeCN/[TBA][BF₄]). Insert: plot of scan rate vs. peak current for reversible redox process of a poly-**12** coated platinum electrode in monomer free electrolyte solution (MeCN/[TBA][BF₄]) [26]. Reproduced by permission of The Royal Society of Chemistry.

before such systems find widespread application in materials science. However, whilst chemical polymerisation techniques are being developed, the insight offered by electropolymerisation is perhaps sufficient to assess the potential of such materials and screen then for future development.

The originaive work of Pickup et al. on polymerisable metal dithiolenes showed **7** to couple by maintaining an oxidising potential sufficient to oxidise the pendent thiophene groups [11]. Growth of the polymer could be achieved by maintaining a current over time. This work was later extended to include other nickel dithi-

olenes, including mixed ligand and unsymmetrically substituted systems and showed that polymer films could also be deposited by potential cycling [31]. Growth of the polymer could be observed in this way by an increase in peak current density of both the forward and reverse sweep upon successive scans (Fig. 5).

Pozo-Gonzalo et al. further extended the field to look at dithiolenes with a terthiophene backbone, in which the central thiophene is fused to the thiolene core (**5**), for systems of nickel, platinum and gold and showed each system to polymerise under potential cycling [12]. Robertson and co-workers showed that copolymer films of nickel dithiolenes with thiophene could be produced, either by holding an oxidising potential, or by potential cycling [13,37]. More recently, they also showed that pendent indole groups could be oxidatively coupled to form a polymer film by potential cycling, thus extending the field beyond thienyl systems [26].

Cathodic polymerisation of a dithiolenes containing pendent phenyl bromide groups (**10**) was also demonstrated by Pickup et al. By cycling to reductive potentials in the presence of a nickel bipyridine catalyst, polymerisation was achieved, thus offering another route into such polymeric systems [31,55].

6. Polymer properties

The properties displayed by the various different polymer systems described above show pronounced differences. These differences allow for an increase in the potential breadth of application of such systems, however, it also means that a fundamental understanding of where the different properties originate from is required if targeted design of new systems is to be achieved. Three possible conjugation modes can be envisaged for the dithiolenes polymers: conjugation predominantly through the metal centre (e.g. for poly-**11** and poly-**12**), conjugation through the ethylene backbone (e.g. for poly-**7**, poly-**10** and poly-**13**) and conjugation through the ligands such that the dithiolenes core remains remote (e.g. for poly-**8** and poly-**14**) (Fig. 6). These different conjugation modes give rise to very different polymer properties.

6.1. Redox properties

The initial work of Pickup et al. on poly-**7** showed the redox properties of the monomer to be preserved upon polymerisation, but with the reduction processes shifted to slightly more positive potentials (Fig. 7) [11]. This was assigned to a change in junction potential on moving to a monomer free solution of a different electrolyte [56]. The group also noted that the reversible oxidation of the dithiolenes core had been lost, or perhaps masked by the shifting of the irreversible thiophene oxidation process to less negative potentials. The more facile p-doping of oligothiophene will shift the oxidation process to less positive potentials, whilst the deposition process would inevitably lead to a more planar geometry, and thus greater electronic communication to the pendent thiophene groups, resulting in a loss in reversibility of dithiolenes core oxidation process. Further work on a similar system, where one of the

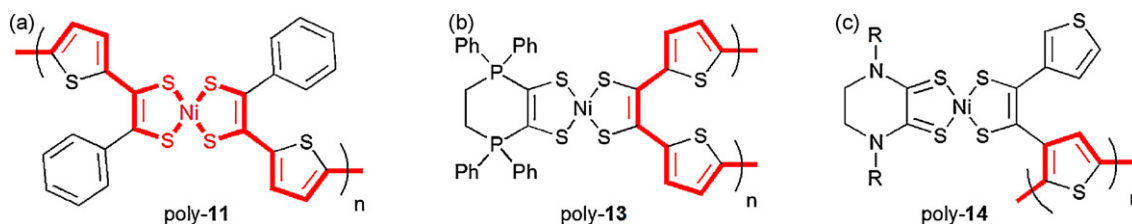


Fig. 6. Proposed conjugation modes for polymerised nickel dithiolenes: (a) conjugation through the metal centre; (b) conjugation through the ethylene backbone; (c) conjugation through the ligand.

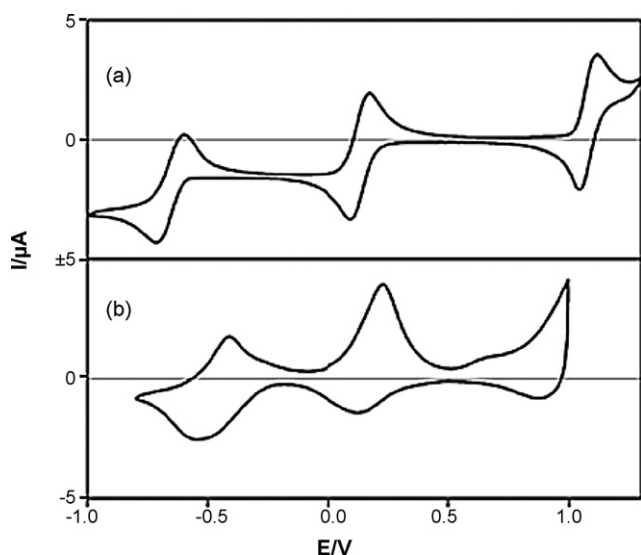


Fig. 7. Cyclic voltammetry (100 mV s^{-1}) of: (a) **7** against a saturated calomel reference, using platinum working and counter electrodes ($\text{DCM}/[\text{TBA}][\text{PF}_6]$) and (b) poly-**7** coated platinum working electrode in monomer free electrolyte solution ($\text{MeCN}/[\text{TEA}][\text{ClO}_4]$) [11]. Reproduced by permission of The Royal Society of Chemistry.

ligand thiophenes was replaced with a phenyl group (**11**), again showed loss of the reversible oxidation process. The nickel centres were shown not to mediate conjugation between the thienyl dimers and thus the loss of this reversible oxidation process was shown conclusively and could therefore be assigned to greater electronic communication to the pendent thiophene groups.

The mixed ligand complex **13** was shown to polymerise under oxidative conditions. The oxidation of this complex, assigned to the NiP_2S_2 core, as well as a reduction process previously outside the electrochemical window, were observed in the polymer film, but only after expanding the scanning window to more oxidising potentials. A conditioning process therefore seemed to be required to activate the film. The reason for this is not fully understood, but might be due to the increased steric crowding imposed by the bulky (dppe) ligand, prohibiting counterion transport through the film [57]. By sweeping to greater potentials, film reconstruction is effected, allowing improved counterion transport through the film.

When a 3-thienyl substituted dithiolenes (**8**) was investigated by Anjos et al., they showed a redox active film to be deposited with some of the dithiolenes redox activity preserved [13]. The extent of polymerisation was limited, it was thought, due to the poor solubility of the neutral complex in MeCN, thus prohibiting greater conjugation lengths from being achieved. This was supported by the complete solubility of the deposited film in DCM, lack of conductivity and little change in absorption spectrum compared with the monomer. When a mixed ligand *bis*-dithiolenes **14a** was investigated, coupling was observed on cycling to positive potentials, resulting in an insoluble polymer film being deposited on the electrode. This suggested that greater chain length had been achieved than for **8**. As in the case of **13**, a conditioning process was also required to activate the polymer film, whereupon characteristic dithiolenes redox processes emerged and remained over many cycles. Both **13** and **14a** possess bulky phenyl groups which might inhibit ingress of more bulky counterions. The redox behaviour of poly-**14a** showed the dithiolenes based oxidation to be largely unchanged upon polymerisation, but the reduction peaks to be shifted to more positive potentials, suggesting that, as for **13**, it was the LUMO (based on the Bz_2pipdt ligand) that was stabilised upon polymerisation. The reason for this is not fully understood and, as such, has only been tentatively assigned to the relative diffi-

culty of incorporation of different counterions into the polymer film [37].

As discussed above, the removal of steric bulk from **12** allowed easier in-plane conformation and hence improved electronic communication with the polymerisable indolyl groups [26] which, upon oxidation, were shown to couple to yield an insoluble polymer. As for **7** and **11**, no conditioning process was required and the resultant polymer displayed almost identical redox behaviour for the two dithiolenes based reduction processes.

Work by Skabara et al. on fused thiophene dithiolenes showed very different redox behaviour of the grown polymer films to that observed in the pendent systems. The films of the nickel, palladium and gold dithiolenes (**9a**, **9b** and **9c** respectively) displayed distinctly polythiophene-like redox behaviour dominated by the polythiophene backbone. In the case of the nickel dithiolenes, some metal based redox behaviour was preserved and resulted in an increase in the oxidation potential of the polythiophene, due to a drawing away of electron density from the polythiophene backbone by the oxidised metal centre. This effect was not observed for the palladium or gold containing systems.

In an effort to tune the properties of polymer systems, Robertson and co-workers have also investigated the effect of copolymerisation. For **8**, copolymerisation with thiophene afforded a more conjugated polymer than was achieved by homo-polymerisation alone, however, the redox behaviour of the resultant film was not investigated [13]. Copolymerisation of **14a** with thiophene also showed greater conjugation in the resultant film. The redox behaviour of this system was shown to be dominated by polythiophene processes, masking, or suppressing the redox behaviour of incorporated dithiolenes [37].

6.2. Optical properties

Given that the polymeric systems in question show such rich and varied redox behaviour, it is perhaps not surprising that the optical properties are equally rich and varied. By growing the polymers directly onto a conductive oxide coated glass electrode (such as FTO or ITO), the optical properties of the less soluble (and more conjugated) polymers can be investigated.

Pickup et al. showed that, for **7**, polymerisation resulted in a red shift of the NIR absorption (1895 cm^{-1}), due to electronic transitions across a reduced HOMO–LUMO gap. This corresponds to the destabilisation of the HOMO upon polymerisation, observed in the redox behaviour of the film by a shift to less positive potentials for the oxidation process. Extensive thiophene linkage was also observed by an increase in the intensity and breadth of the transitions in the UV/vis region [11].

For systems where a conjugated polymer backbone is limited, such as in **12**, negligible red shifting of the NIR absorption is observed as HOMO destabilisation is limited by the restraints imposed on the conjugation length [26].

Mixed ligand dithiolenes, where the polymerisable units are capable of forming extensive conjugated chains, such as for **14**, show a pronounced shift in the NIR absorption upon polymerisation (4360 cm^{-1}) [37]. This is due to the stabilisation of the LUMO upon polymerisation, observed in the redox behaviour of the film by a shift to less negative potentials for the reduction processes. This is indicative of extensive electronic communication between the dithiolenes core and the polymer backbone. Interestingly, the shift in the NIR absorption was shown to be tuneable by copolymerisation with thiophene. By adding an equimolar amount of thiophene, the shift in the NIR was reduced to 3495 cm^{-1} .

Polymers of fused thiophene nickel dithiolenes systems (poly-**9a**) do not show an appreciable shift in the NIR absorption, as for the pendent tetrathienyl system (poly-**7**), but instead show a very broad absorption over the entire visible and NIR window

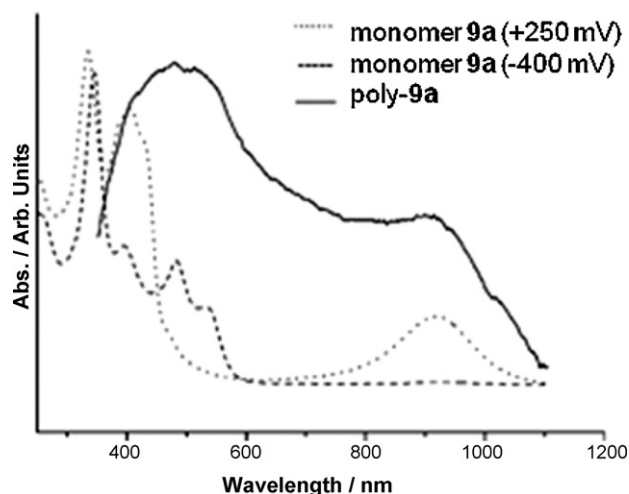


Fig. 8. Electronic absorption spectra of **9** in its dianionic (dashed line) and anionic (dotted line) oxidation state generated electrochemically in an OTTE cell (MeCN/[TBA][PF₆]), as well as poly-**9** as a thin film on ITO glass (solid line) [58]. Reproduced by permission of The Royal Society of Chemistry.

(400–1000 nm) (Fig. 8). This is due to a reduction in the energy of the π – π^* transition in the polymer backbone, and results in a bathochromic shift of the triaryl unit absorptions upon polymerisation. For the palladium and gold containing systems, the dithiolenes remain electronically isolated during polymerisation and, as a result, no dithiolenes based NIR absorption is observed for either polymer, and thus the absorption spectra is more reminiscent of other poly(terthiophene)s [59].

6.3. Conductive properties

No thorough investigation of the conductive properties of dithiolenes containing polymers has been performed, however, some preliminary data are available from impedance spectroscopy and the growth of polymers onto interdigitated electrodes and have shown poly-**7** and poly-**9** to have p-type conductivities in the range 10^{-4} to 10^{-6} S cm⁻¹. Though initially disappointing, these data represents preliminary work on non-optimised systems and should thus be considered as a benchmark limit for future optimisation.

6.4. Switching behaviour

The observed redox functionality of the polymers, combined with the interesting optical properties, has prompted some groups to investigate how the optical properties behave under an applied voltage.

Pickup et al. showed that, for poly-**7**, the NIR absorption could be switched off by holding a potential sufficient to completely fill the LUMO orbital. The typical low-energy HOMO to LUMO transition of the neutral and monoanionic species was then not observed and the resulting absorption spectrum was limited to the π – π^* transitions of the polythiophene backbone, which cuts off at ~750 nm.

This behaviour was also observed by Robertson et al. for poly-**12**, however, as extensive conjugation of the indole backbone was restricted, a large part of the visible spectra remained transparent [26]. This study went further to look at the sequential filling of the LUMO. It was shown that the NIR absorption could be switched over three absorbing states: absorbing, reduced absorption and transmissive upon varying the potential (Fig. 9). Both switching processes were shown to be reversible, however, the speed of switching was limited in the second reduction due, it was thought, to the steric constraints of incorporating two bulky [TBA] counterions into the film. For such a system to be useful, fast switching and

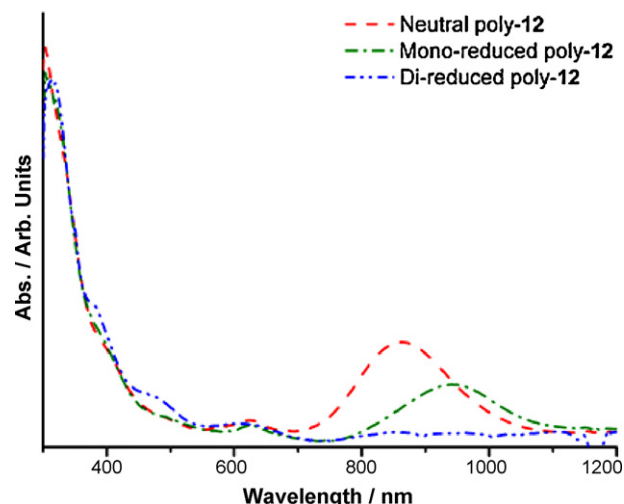


Fig. 9. Electronic absorption spectra of a poly-**12** coated FTO glass electrode in the neutral, mono- and di-reduced state generated electrochemically in an OTTE cell (MeCN/[TBA][BF₄]) [26]. Reproduced by permission of The Royal Society of Chemistry.

good stability are prerequisites [60]. Reversible switching of the absorption intensity of poly-**12** at 860 nm was observed by switching the applied potential between 0.3 V and –0.4 V and showed the absorption to vary with only minimal loss in peak absorption over 100 cycles.

For fused thiophene nickel dithiolenes systems, it appears that the NIR absorption can be tuned by oxidation at ~1 V, resulting in a hypsochromic shift of the NIR band. This process seems to be dithiolenes based as the polythiophene π – π^* transitions remain unchanged upon doping. For the palladium and gold containing systems (**9b** and **9c**), oxidation results in a broad band forming ~1050 nm. This was assigned to the formation of polarons/bipolarons in the polythiophene chain and not a dithiolenes based redox process.

Such switchable systems might find application in the telecommunications field as a variable optical attenuator (VOA) [61]. Switching of signal transmission intensity in the NIR region (800–2000 nm) is useful in signal modulation for silica fibre-optics as they are most transparent in the NIR region [53].

7. Summary and future outlook

The field of polymerisable metal dithiolenes is small but evolving fast. Already, some interesting results have been obtained and the potential for such systems to be incorporated into functional devices is already being realised. The aim of this review is to identify the effect of structural and processing factors of the monomer on the properties of the resultant polymeric materials so as to promote the targeted design of new systems in an effort to help realise the full potential of polymeric dithiolenes based materials:

- By designing ligand systems that form conjugated polymer chains with pendent metal complex units, the redox processes of the symmetrical dithiolenes can remain intact, whilst the optical properties display a distinct red shift in the low energy NIR transition.
- By designing ligand systems where linkage is necessarily through the metal centres, extensive conjugation is restricted and both the redox and optical properties remain largely unchanged, thus stabilisation of the dithiolenes in a robust organic film is achieved. Therefore, the position of attachment of the pendent group is

crucial as it determines whether the dithiolene complex is part of the polymer main chain or attached as a side group.

- For mixed ligand systems, the effect of polymerisation is to preserve, yet modify, the discrete redox and optical properties, such that the HOMO–LUMO separation is reduced, resulting in discrete, very low energy NIR transitions. In principle this allows continuous tuning of the optical properties by control of the copolymerisation ratio.
- By fusing a dithiolene to a thiophene backbone, the redox and optical properties of the resultant film are dominated, in some cases entirely, by the polythiophene backbone, showing broad absorption covering a substantial part of the spectrum.

Future work on such systems will most likely focus on specific applications of these polymeric materials. For example, the fused thiophene systems will no doubt be optimised for photovoltaic and smart window application due to the broad and switchable absorption displayed by these systems. The more discrete redox and optical properties of the pendent dithiolene systems will most likely be optimised for optical switching applications, such as Q-switching NIR laser dyes or variable optical attenuators.

Many challenges remain ahead; the most pressing of which is how production of these materials can be scaled-up. Electropolymerisation methods, although suitable for small scale niche applications that involve direct modification of electrodes, are unsuitable for bulk processing, thus more conventional chemical polymerisation methods must be explored for these systems to reach their full potential.

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