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Near-infrared electrochromic materials for optical attenuation based on transition-metal coordination complexes

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Abstract Redox-active transition-metal complexes which show strong changes in their electronic spectra in the near-infrared (NIR) region in different oxidation states are attracting increasing interest as NIR electrochromic dyes for electro-optic switching at the wavelengths used for silica-based optical telecommunications networks. This brief review surveys recent work in the field based on ruthenium(II)-dioxolene, tris(pyrazolyl)borato-molybdenum(V) and mixed-valence Ru(II)-Ru(III) complexes, which all show strong NIR electrochromism and have been incorporated into prototypical devices such as the variable optical attenuator by attachment to transparent electrodes, either by adsorption or polymerisation.

which undergo a strong change in their optical properties when doped with electrons or holes, i.e. the redox change is not necessarily stoichiometric but partial. Molecular species have been considerably less exploited for their electrochromic properties; amongst the first examples are the viologen-based systems of Fitzmaurice [8], when anchored to a conducting substrate, turn from colourless to blue or green following a reversible one-electron reduction to the viologen radical anion. Because the spectral change is so marked and lies in the visible region, these systems have potential as reusable display devices.

Recently a few groups have become interested in the electrochromic properties of transition metal complexes in the near-infrared (NIR) region (typically, 800–2,000 nm). The NIR region is of particular significance because the ‘telecommunications windows’—the wavelengths at which silica optical fibres are most transparent, and which are accordingly used for propagation of signals through fibre-optic networks—lie in the 1,300 to 1,550-nm region. Materials which display electrochromism in this region are accordingly of interest for electro-optic switching, whereby an electrical input (an applied redox potential) is used to effect modulation of light transmission at these wavelengths. A device which can be constructed using these principles is a variable optical attenuator (VOA), [9–11] which is important in optical telecommunications networks because it can be used to compensate for power variations in the signal caused by other components in the circuit.

It is becoming apparent from recent studies in several groups that transition-metal complexes are of particular value in this field, for several reasons. Firstly, it is a common characteristic of transition-metal complexes that they often show reversible electrochemical behaviour. Secondly, some complexes are very strongly electrochromic in the NIR region due to charge-transfer transitions, with changes in extinction coefficient from zero to tens of thousands following a simple one-electron redox change. Thirdly, fine-tuning is possible by modifying co-ligands or ligand substituents such that

Introduction

Electrochromism—a change in colour associated with a change in oxidation state—has been of interest for several decades [1–3]. The phenomenon applies to the control of both light transmission (windows) and reflection (mirrors), and has applications in fields as diverse as switchable display devices [4], smart windows which can filter out different amounts of light according to the prevailing conditions [5], variable-reflectance car mirrors [1] and controlling the thermal emission signature of spacecraft and satellites [6].

The vast majority of materials used in the field of electrochromism are either metal oxides [7], cyanometallates (e.g. Prussian Blue), [3] or conducting polymers, [7]

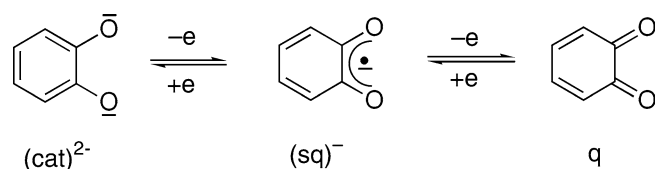
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redox potentials and spectroscopic absorption maxima can be controlled with a high degree of confidence. Finally, it is possible in many cases to functionalise the complexes with substituents which will allow them to be incorporated into thin films, either by polymerisation or by adsorption onto a nanocrystalline metal oxide surface.

This review accordingly describes recent developments in the field of NIR-electrochromic transition-metal complexes, and their incorporation into prototypical devices such as a VOA.

Ruthenium(II) dioxolene complexes

Lever [12] described in 1986 the mononuclear complex $[\text{Ru}(\text{bipy})_2(\text{cat})]$ (bipy = 2,2'-bipyridine), which has no NIR absorptions. It undergoes however two reversible oxidations which are ligand-centred cat/sq and sq/q couples (where 'cat', 'sq' and 'q' are abbreviations for catecholate, 1,2-benzoquinone monoanion, and 1,2-benzoquinone respectively; see Scheme 1); in the two



Scheme 1 The catecholate/semiquinone/quinone redox series

oxidised forms, the presence of a 'hole' in the dioxolene ligand results in the appearance of $\text{Ru}(\text{II}) \rightarrow \text{sq}$ and $\text{Ru}(\text{II}) \rightarrow \text{q}$ MLCT transitions, the former at 890 nm and the latter at 640 nm with intensities of ca. $10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The cat/sq and sq/q couples accordingly result in modest NIR electrochromic behaviour, with the interconversion between $\text{Ru}(\text{II})/\text{cat}$ and $\text{Ru}(\text{II})/\text{sq}$ states being most significant as it results in the reversible appearance/disappearance of an absorption at 890 nm [12].

Whilst this mononuclear complex on its own shows only modest NIR electrochromism, Ward [13] showed that the NIR transitions become far more impressive when two or more of these chromophores are linked by a conjugated bridging ligand, as in $[1]^{n+}$ ($n=0-4$). This complex is based on a 'back-to-back' bis-catecholate ligand; assuming that each terminus has two redox interconversions (cat/sq and sq/q couples, as before), we expect four redox processes linking the members of a five-membered redox series. This was indeed shown to be the case (Fig. 1), with the ligand-based redox processes spanning the fully reduced (cat-cat) to fully oxidised (q-q) states and all members in between. Of particular note is the central sq-sq state, which is diamagnetic because the two semiquinone fragments are coupled to give an additional double bond between the

two rings, which makes the ligand planar in this state. In the state $[1]^{2+}$ (with the bridging ligand being sq-sq), the NIR absorption, arising from a $\text{Ru}(\text{II}) \rightarrow \text{sq}$ MLCT transition involving the bridging ligand, is at 1,080 nm with $\epsilon = 37,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (Fig. 2a). In the state $[1]^{3+}$ (with the bridging ligand being sq-q), the absorption is red-shifted to 1,225 nm and is equally intense. The NIR MLCT transition however disappears in the fully reduced form [1], and moves into the visible region in the fully oxidised form $[1]^{4+}$, so redox interconversions of this compound (e.g. Fig. 2b) offer much better possibilities for NIR electrochromism than do the mononuclear $[\text{Ru}(\text{bipy})_2(\text{cat})]$ complex [9] on which it is based.

Similarly, the dinuclear complex $[2]^{n+}$ ($n=1-4$), in which the bridging ligand is a trihydroxyfluorone unit with two chelating dioxolene-like binding sites, shows three reversible, one-electron, ligand-centred redox processes [14]. Again, ligand-based oxidation results in low-energy 'holes' in the π -system resulting in $\text{Ru}(\text{II}) \rightarrow$ bridging ligand MLCT transitions in the

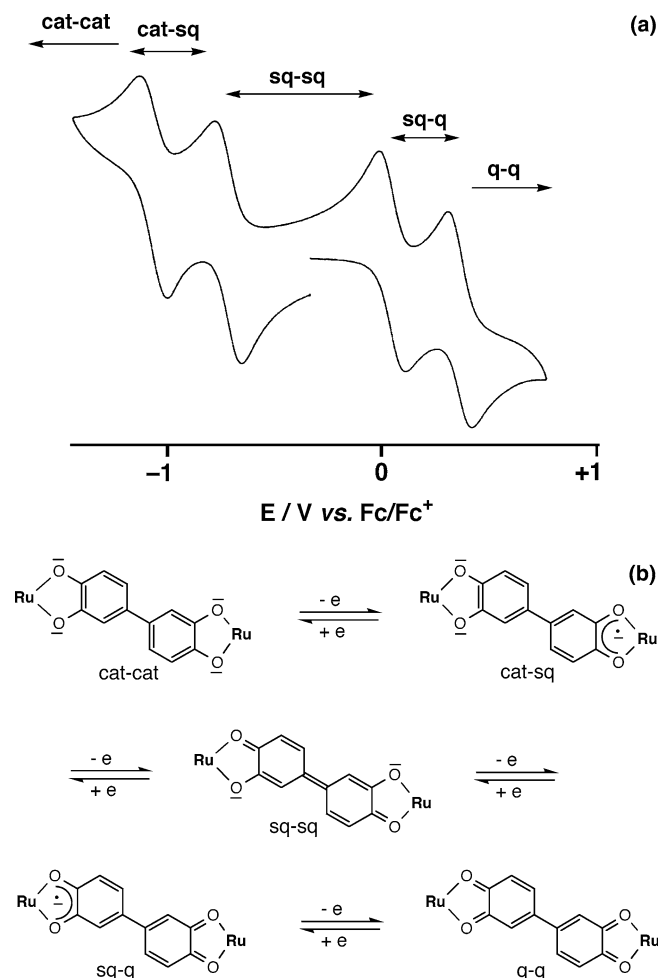


Fig. 1 a Voltammogram showing the four reversible redox interconversions of the redox series $[1]^{n+}$ ($n=0-4$); b the nature of the bridging ligand in each oxidation state

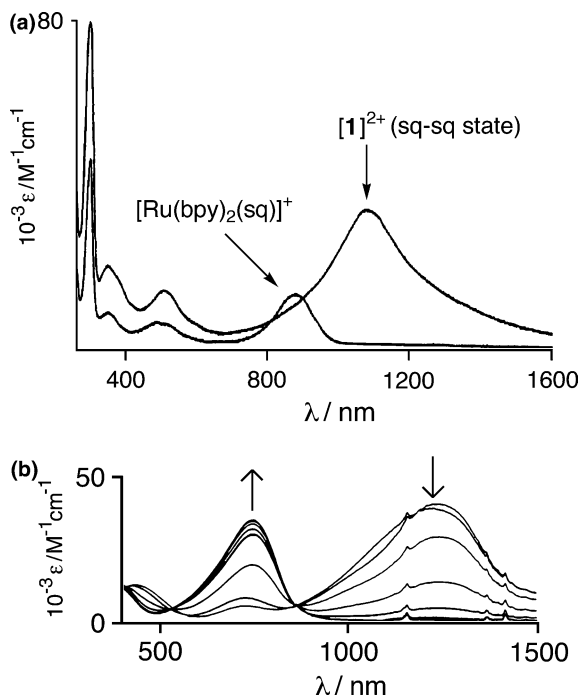


Fig. 2 **a** Comparison of the electronic spectra of $[\text{Ru}(\text{bpy})_2(\text{sq})]^+$ and $[1]^{2+}$ in MeCN. **b** Spectroscopic changes associated with the $[1]^{3+}/[1]^{4+}$ couple in MeCN (the near-IR absorption at around 1,300 nm belongs to $[1]^{3+}$ and disappears during one-electron oxidation)

oxidised species. Thus form $[2]^+$ (ligand fully reduced) has no absorptions at wavelengths longer than 900 nm, whereas $[2]^{2+}$ and $[2]^{3+}$ have absorption maxima at $\approx 1,650$ and $1,230$ nm, respectively, the latter being particularly intense (Fig. 3). Thus, the complex is *polyelectrochromic*, with a large number of stable oxidation states accessible in which the absorption maxima of the NIR MLCT transitions, involving the oxidised forms of the bridging ligand, are redox-dependent. The trinuclear

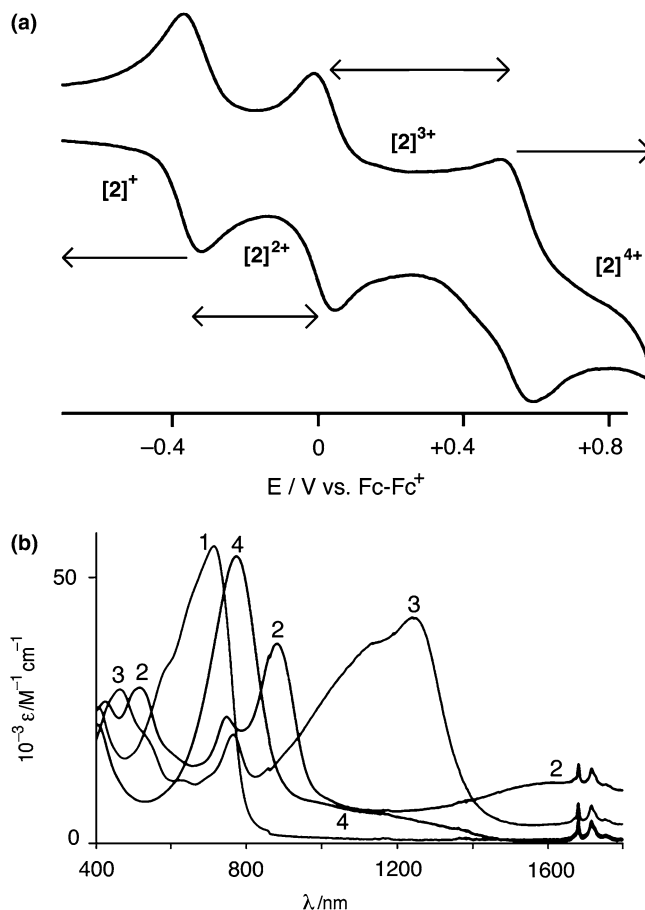
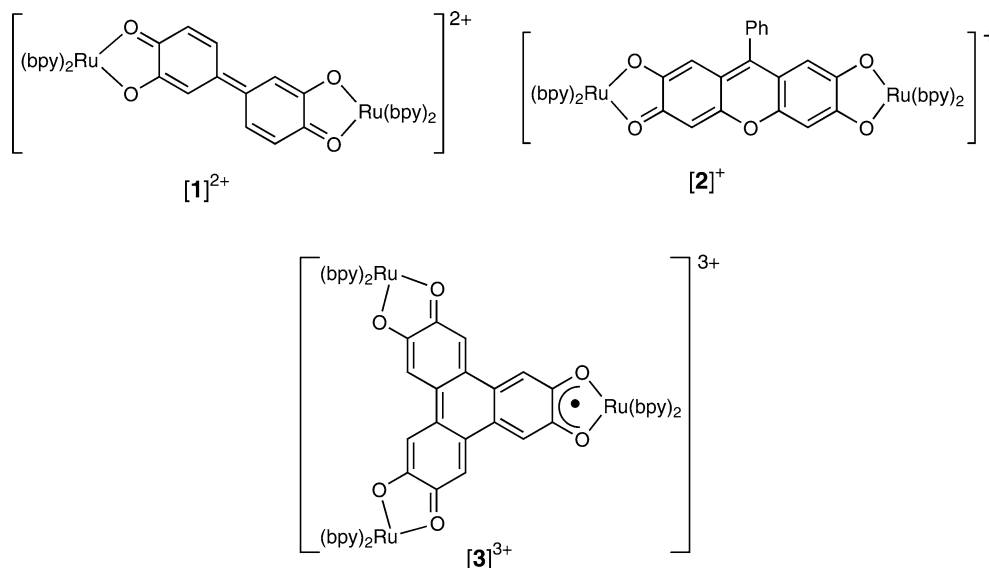


Fig. 3 **a** Voltammogram showing the three reversible redox interconversions of the redox series $[2]^{n+}$ ($n = 1-4$). **b** Electronic spectra in the four different oxidation states (in MeCN; the numbers 1, 2, 3, 4 refer to the charge n +)

complex $[3]^{n+}$ ($n = 3-6$), based on the bridging ligand hexahydroxytriphenylene, is also polyelectrochromic, existing in four stable redox states based on redox

Structure 1-3



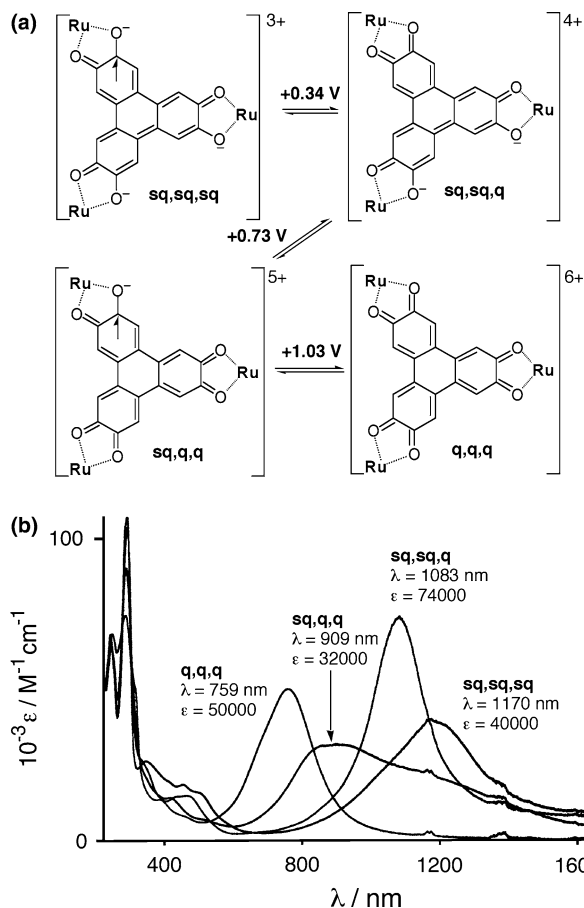


Fig. 4 **a** The ligand-based redox interconversions of [3]ⁿ⁺ (*n* = 3–6). **b** Electronic spectra of the members of the redox series [3]ⁿ⁺ (*n* = 3–6) in MeCN

interconversions of the bridging ligand (from sq-sq-sq to q-q-q; Fig. 4a) [15]. The Ru(II) → bridging ligand MLCT transition moves steadily from 1,170 to 759 nm, with intensities of up to 70,000 dm³ mol⁻¹ cm⁻¹, as the ligand undergoes stepwise one-electron oxidation (Fig. 4b).

The impressive NIR electrochromic behaviour of these Ru(II)-dioxolene complexes has led to some of them being incorporated into ‘electrochromic windows’ in which the complex units are adsorbed onto a nanocrystalline, conducting, Sb-doped SnO₂ surface via carboxylate anchors on the terminal bipy ligands, in a similar manner to that well developed in Grätzel-type solar cells. The first example was based on complex 4 [16, 17], which contains four carboxylic acid anchoring groups at the periphery of the complex, and used tetrachlorocatechol as the dioxolene unit instead of catechol, which shifts the cat/sq redox potential to a more positive value such that it lies within the conducting potential window of the SnO₂:Sb. A modified electrode was simply prepared by adsorption of complex 4 from alcoholic solution onto a nanocrystalline SnO₂:Sb film which was in turn deposited on an ITO surface. The high effective surface area of the SnO₂:Sb particles resulted in

high loading of the electrochromic dye and a strong colour to the electrode. Figure 5 shows that the reversible cat/sq couple of the dye is preserved on the modified electrode surface (using MeCN/Bu₄NPF₆ as solvent and base electrolyte, which does not desorb the complex). On sweeping the applied potential from negative to positive through the redox potential, a rapid colour change is observed in the visible region (blue–gray to pink), as well as a decrease in transmittance at 940 nm of about 30% associated with the appearance of the Ru(II) → sq MLCT transition when the dioxolene ligand is oxidised. These changes are reversible when the potential sweep is reversed. The switching occurs with a time constant of about 0.5 s, i.e. the colour changes are >99% complete in 1.5 seconds, and the system accordingly acts as both a visible and an NIR electrochromic window based on a single cat/sq redox interconversion at a modest potential.

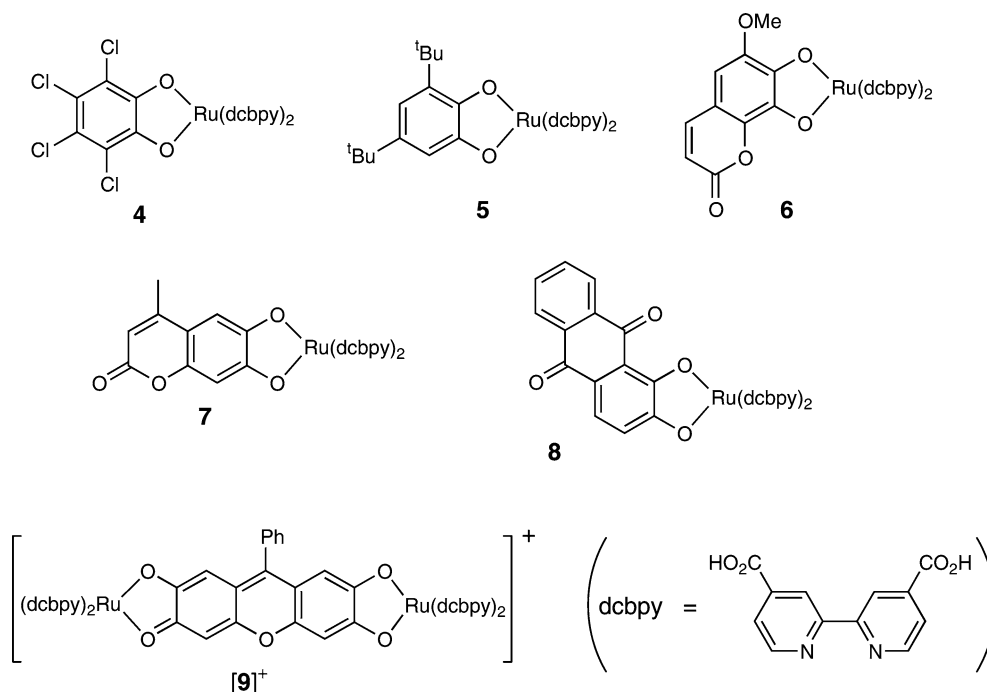
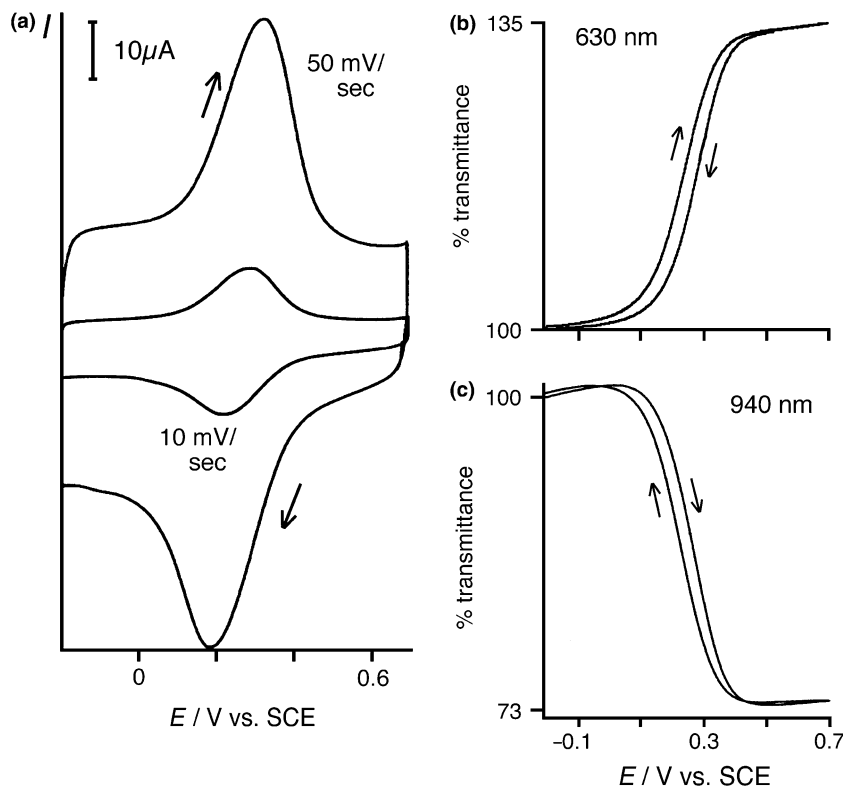
Similar examples of mononuclear Ru(II)-dioxolene derivatives showing comparable NIR electrochromic behaviour were developed by Schwab et al. [18] who examined complexes 5–8; these are all relatives of Lever’s original compound [Ru(bpy)₂(cat)] but with different dioxolene ligands, and bearing carboxylic acid substituents which allow attachment of the molecules to a transparent, nanocrystalline SnO₂:Sb film. As Ward and co-workers observed with complex 4, adsorption onto the electrode surface has little effect on the redox potentials and the electronic spectra, and oxidation of the reduced (catecholate) forms of these complexes to the semiquinone forms resulted in NIR electrochromism of the films in the 900-nm region in every case because of the appearance/disappearance of the Ru(II) → sq MLCT transition.

Complex [9]⁺ is an analogue of [2]⁺ but decorated with peripheral carboxylic acid units so that it too could be attached to an SnO₂:Sb surface. On such a modified electrode, the first two ligand-based redox processes remained accessible, and sweeping the applied potential from negative to positive resulted in changes in the absorption spectrum of the ‘window’ similar to those seen for the parent complex [2]ⁿ⁺ in solution (Fig. 6). In particular, oxidation of the dye results in a decrease in absorbance in the 600 to 750-nm region, resulting in a pronounced colour change from deep blue to pink, and also an increase in absorbance across the NIR region (1,000–1,500 nm) as the adsorbed complex is oxidised in steps from [9]⁺ to [9]³⁺ [19, 20].

Tris(pyrazolyl)borato-molybdenum complexes

The mononuclear oxo-Mo(V) complex 10 [Mo(Tp*)(O)Cl(OPh)] [Tp* = hydrotris(3,5-dimethylpyrazolyl)borate], first reported by Enemark [21] undergoes reversible one-electron Mo(VI)/Mo(V) and Mo(V)/Mo(IV) redox interconversions at easily accessible potentials [22]. Whilst reduction to the Mo(IV) state results in unremarkable changes in the electronic

Fig. 5 **a** Cyclic voltammogram of complex 4 adsorbed on a nanocrystalline Sb-doped SnO₂ electrode, showing the ligand-centred cat/sq couple. **b** Change in transmission of the 'window' at 630 nm during a redox cycle. **c** Change in transmission of the 'window' at 940 nm during a redox cycle



Structure 4-9

spectrum, oxidation to Mo(VI) results in the appearance of a low energy phenolate \rightarrow Mo(VI) LMCT process at 681 nm with $\epsilon = 13,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ [23]. This is rather unremarkable from the point of view of NIR electrochromism but, as with the Ru-dioxolene complexes described above, when polynuclear analogues are

prepared based on extended aromatic bridging ligands with two or more binding sites, the electrochromic behaviour becomes much more interesting.

McCleverty, Ward et al. prepared and examined an extensive series of dinuclear complexes of the form $[\text{Mo}(\text{Tp}^*)(\text{O})\text{Cl}_2(\mu\text{-OC}_6\text{H}_4\text{EC}_6\text{H}_4\text{O})]$, in which

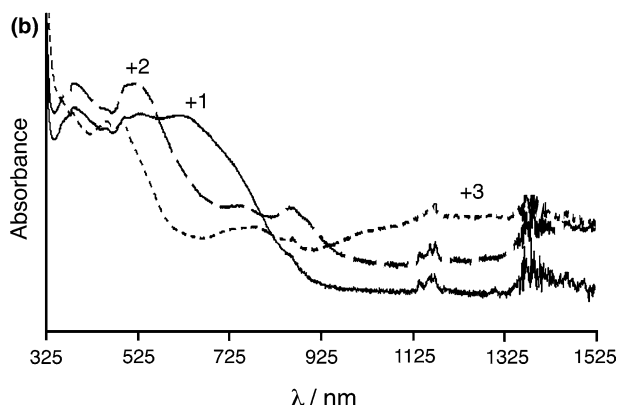
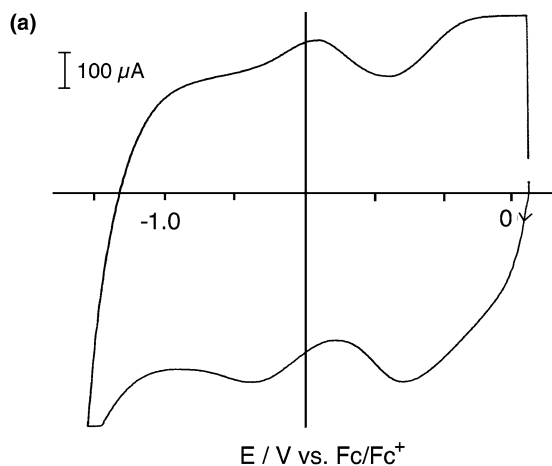


Fig. 6 **a** Cyclic voltammogram of complex $[9]^+$ adsorbed on a nanocrystalline Sb-doped SnO_2 electrode, showing the first two ligand-centred redox couples (cf. Fig. 3a). **b** Changes in electronic spectra of the $[9]^{n+}$ -based 'window' ($n = 1-3$) as a result of the two redox processes

two oxo-Mo(V) fragments are connected by a bis-phenolate bridging ligand in which a conjugated spacer E separates the two phenyl rings[23–25]. In these complexes, the electronic interaction between the two metals results in a separation of the two Mo(V)/Mo(VI) couples, such that the complexes can be oxidised from the Mo(V)–Mo(V) state to Mo(V)–Mo(VI) and then Mo(VI)–Mo(VI) in two distinct steps, with the

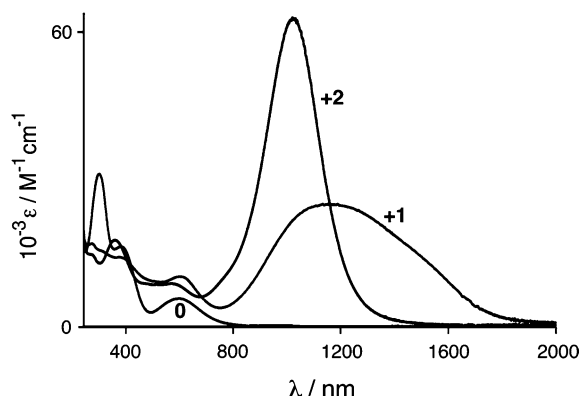
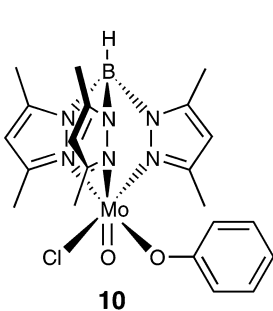


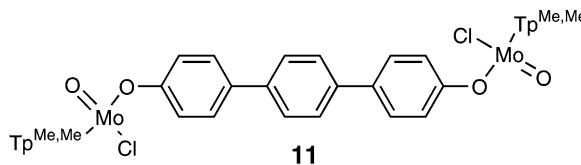
Fig. 7 Electronic spectra of the redox series $[11]^{n+}$ ($n = 0-2$) in CH_2Cl_2

intermediate mixed-valence state having a high comproportionation constant and being stable over a wide redox potential range. It was found that in the oxidised forms of the complexes, containing one or two Mo(VI) centres, the LMCT transitions are at lower energy and of much higher intensity than in the mononuclear complexes (complex 11 gives a representative example, in Fig. 7), because the double negative charge on the bridging ligand raises the energy of the π -donor HOMO, reducing the energy of the LMCT transition. Depending on the nature of the group E in the bridging ligand, the absorption maxima can span the range 800–1,500 nm, with extinction coefficients of up to $50,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

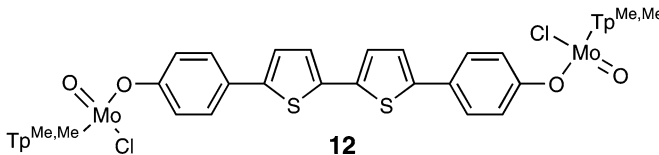
A prototypical device to illustrate the possible use of these complexes for modulation of NIR radiation in a VOA has been described[26]. A thin-film cell was prepared containing a solution of complex 12, where the spacer E is a bithienyl fragment, and base electrolyte between transparent, conducting glass slides. Complex 12 develops an LMCT transition at 1,360 nm ($\epsilon = 30,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) on one-electron oxidation to the Mo(V)–Mo(VI) state $[12]^+$, which is completely absent in the Mo(V)–Mo(V) state. Application of an alternating potential, stepping between +1.5 V and 0 V for a few seconds each, resulted in fast switching on/off of the NIR absorbance reversibly over several



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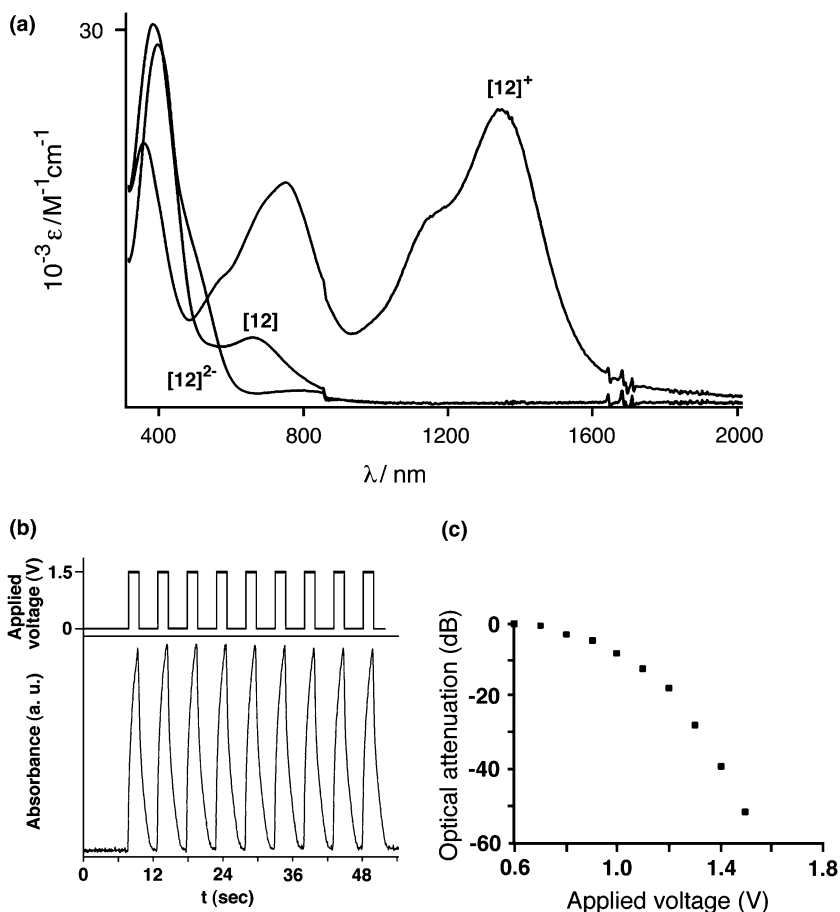


11



12

Fig. 8 **a** Electronic spectra of $[12]^{n+}$ ($n = -2, 0, +1$) in CH_2Cl_2 . **b** Reversible changes in optical absorption at 1,160 nm of $[11]/[11]^+$ in a thin-film cell using an applied voltage cycled between 0 V (3 s) and +1.5 V (2 s). **c** Optical attenuation of a 1,300-nm laser as a function of applied voltage in a cell based on $[11]/[11]^+$



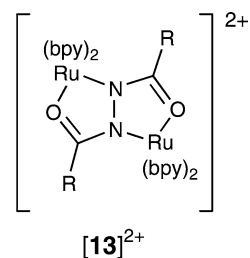
thousand cycles. A larger cell was used to show how a steady increase in the applied potential of the solution, which resulted in a larger proportion of the material being oxidised, allowed the intensity of a 1,300 nm laser to be attenuated reversibly and controllably over a dynamic range of 50 dB (a factor of *ca.* 10^5): the cell accordingly acts as an NIR variable optical attenuator (Fig. 8). The disadvantage of this prototype is that, being solution-based, switching is relatively slow compared to thin films or solid-state devices, but the optical properties of these complexes show great promise for further development. It is a significant limitation of these materials, however, that the complexes do not lend themselves to further functionalisation, in contrast to the bipy-based complexes (above). Attachment of pendant carboxylic acid groups to a tris(pyrazolyl)borate ligand, for example, is unknown, in comparison with the ready availability of 2,2'-bipyridine-4,4'-(CO_2H)₂ which is used for attachment of bipy-based complexes to metal oxide supports.

Mixed-valence dinuclear complexes

It has been known since the discovery of the Creutz-Taube ion [27] that dinuclear complexes in which there is

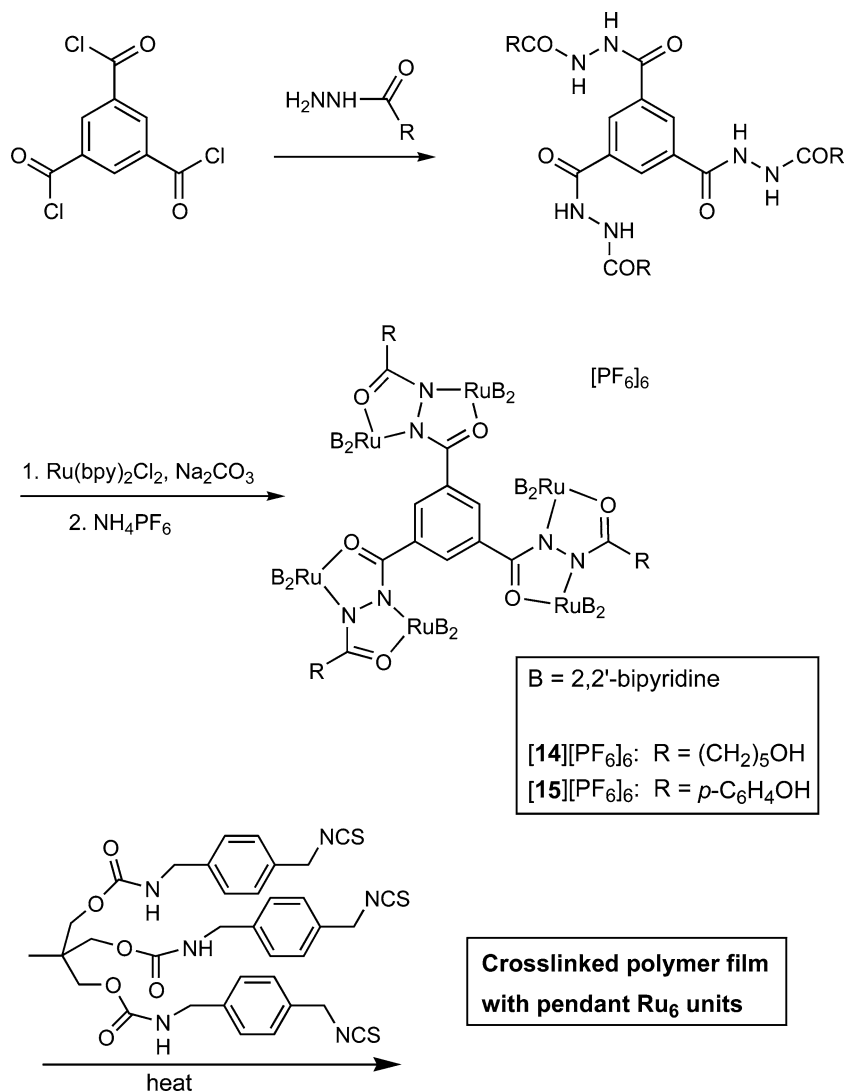
a significant metal–metal electronic coupling can show, in their mixed-valence state, an inter-valence charge-transfer (IVCT) transition from the electron-rich to the electron-poor metal terminus. In a significant number of cases, these IVCT transitions occur in the NIR region and are very intense; [28] since such transitions are (by definition) absent in the iso-valent states, such complexes are excellent candidates for the preparation of NIR electrochromic materials and devices. It is only very recently, however, that this possibility has begun to be exploited.

Wang and co-workers have shown in the last few years how a dinuclear Ru(II) complex unit, which shows a strong IVCT transition when oxidised to the



Structure 13

Scheme 2 Preparation of hexanuclear complexes [14][PF₆]₆ and [15][PF₆]₆ and their copolymerisation with a tris-isocyanate



Ru(II)–Ru(III) state, can be incorporated into polymer films attached to a transparent, conducting substrate (ITO). The basic complex unit is [13]²⁺ in which two Ru(bipy)₂⁺ are connected by a 1,2-dicarbonylhydrazido (DCH) bridging ligand [29]. Very short bridging ligands of this nature are ideal at affording strong electronic coupling between metal centres and a consequently intense IVCT transition: depending on the substituents R attached to the DCH bridging ligand, the IVCT absorption maximum in the Ru(II)–Ru(III) state lies between 1,350 nm and 1,650 nm (exactly spanning the two telecommunications windows of silica) with an extinction coefficient of ca. 20,000 M⁻¹ cm⁻¹.

In order to (1) maximise the optical density, and (2) provide reactive peripheral functional groups for copolymerisation of the electrochromic molecules, three such dinuclear units were incorporated into a single molecule according to the method in Scheme 2 [29–31]. These Ru₆ compounds [14]⁶⁺ and [15]⁶⁺ also contain reactive hydroxyl groups in the form of alcohol or phenol substituents, which allow copolymerisation with a tri-isocyanate to give a cross-linked polymer based on

robust urethane linkages. Accordingly, a solution containing a mixture of [14][PF₆]₆ or [15][PF₆]₆ and the cross-linking tris-isocyanate agent was deposited onto ITO by spin-coating to give an even film (≈400 nm thick), which was heated to induce the polymerisation and immobilise the electrochromic complex. The resulting modified electrodes showed redox behaviour very similar to that of the free complexes in solution, with two well-separated Ru(III)/Ru(II) couples. Application of a potential more positive than the first Ru(III)/Ru(II) couple resulted in rapid (seconds timescale) appearance of the IVCT transition and consequent attenuation of NIR radiation directed through the window (Fig. 9). The switching was reversible over several thousand cycles with only a slight loss in performance, with a switching time of around 2 s; an attenuation of about 3dB at 1,550 nm was attained in the best case [31].

A slightly different approach was taken by Bigozzi and co-workers [32] who prepared asymmetric dinuclear complexes 16–19, which contain a carboxylate unit attached to the terminal pyridine ligand. In these

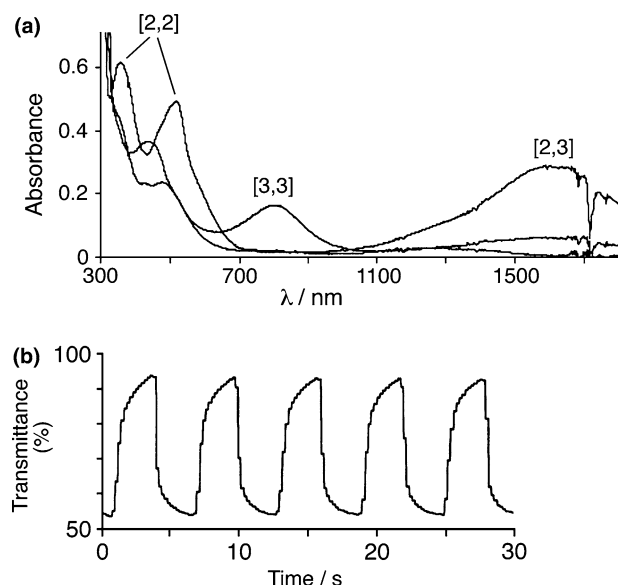
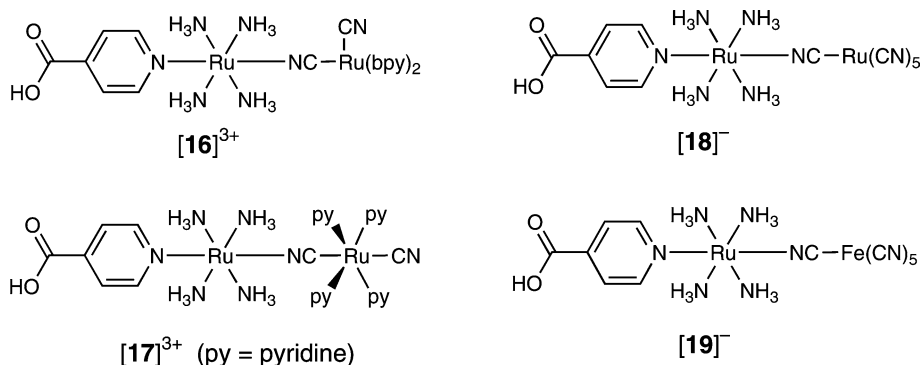


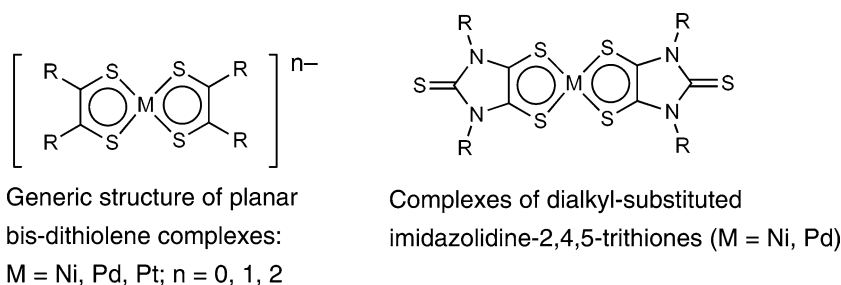
Fig. 9 **a** Electronic spectra of a thin-film electrochromic window based on polymerised complex $[15]^{6+}$ (see Scheme 2) on an ITO substrate; the figures in brackets denote the Ru oxidation states in each Ru_2 unit, such that [2,3] denotes the mixed-valence Ru(II)–Ru(III) state. **b** Variation of transmittance at 1,550 nm for the ‘window’ as the compound is cycled between the [2,2] and [2,3] states by alternation of the applied potential

complexes, the two components are linked by a cyanide bridge, and the Ru-ammine unit has a Ru(III)/Ru(II) couple at a potential close to 0 V. In the reduced forms, the M(II)–Ru(II) complexes show no NIR absorption, but on oxidation of the Ru-ammine unit to Ru(III), a M(II) \rightarrow Ru(III) IVCT transition appears

Structure 16-19



Scheme 3 Dithiolene-based NIR electrochromic compounds



between 763 nm (for 16) and 1,149 nm (for 19). This behaviour occurs both in solution and with the complexes adsorbed onto transparent $SnO_2:Sb$ or TiO_2 electrodes via the carboxylate anchor, with switching times in these systems on the millisecond timescale for the immobilised films. These compounds also show pronounced visible colour changes in the different oxidation states and are accordingly visible as well as NIR electrochromes.

Conclusions

The purpose of this brief review has been to highlight recent progress in the use of NIR-electrochromic transition metal complexes in materials and devices. In general, the basic optical properties of the chromophores, especially mixed-valence ruthenium complexes, have been known for decades; only very recently, however, has attention turned to incorporation of these complexes, with their desirable electrochromic properties, into prototype devices for NIR optical attenuation. The two principal methods that have been used to immobilise the electrochromes on transparent conductive support are (1) adsorption onto a metal oxide film using carboxylate anchors, and (2) chemical polymerisation. Great scope exists for the exploitation of other complexes with comparable optical properties in this field. One obvious example is the extensive series of Ni, Pd and Pt dithiolene complexes of general types shown in Scheme 3, which have long been known to have intense NIR absorptions in the neutral and monoanionic states, but not in the fully reduced dianionic state [3, 33–36].

Applications of these have focussed largely on exploiting the absorbance in a single oxidation state, such as Q-switching of lasers [33, 34] and use as NIR-sensitive photocurrent detectors [37], rather than on the *difference* in absorbance as a result of a redox change. Given the remarkable optical properties of these series of complexes, however, there is plenty of scope for exploitation of dithiolenes complexes in NIR electrochromic materials and devices.

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Appendix

Since this review was submitted, Ward and co-workers have described the use of complex [2]⁺ directly deposited from solution as a thin film onto an ITO surface as a NIR electrochromic window, with good stability and fast switching times [38].

References

- Mortimer RJ (1997) *Chem Soc Rev* 26:147
- Rosseinsky DR, Mortimer RJ (2001) *Adv Mater* 13:783
- Mortimer RJ, Rowley NM (2003) Metal complexes as dyes for optical data storage and electrochromic materials. In: Ward MD (ed) *Comprehensive coordination chemistry*, 2nd edn, vol. 9. Elsevier, Oxford, pp 581–619
- Pages H, Topart P, Lemordant D (2001) *Electrochim Acta* 46:2137
- Cui HN, Costa MF, Teixeira V, Porqueras I, Bertran E (2003) *Surf Sci* 532:1127
- Chandrasekhar P, Zay BJ, McQueeney T, Scara A, Ross D, Birur GC, Haapanen S, Kauder L, Swanson T, Douglas D (2003) *Synth Met* 135:23
- See *Electrochimica Acta* (1999) 44, issue 18 (special issue devoted to electrochromic materials)
- Cummins D, Boschloo G, Ryan M, Corr D, Rao SN, Fitzmaurice D (2000) *J Phys Chem B* 104:11449
- Barber B, Giles CR, Askyuk V, Ruel R, Stulz L, Bishop D (1998) *IEEE Photo Technol Lett* 10:1262
- Kawai T, Koga M, Okuno M, Kitoh T (1998) *Electron Lett* 34:264
- Jin Y-S, Lee S-S, Son Y-S (1998) *Electron Lett* 35:916
- Haga M, Dodsworth ES, Lever ABP (1986) *Inorg Chem* 25:447
- Joulié LF, Schatz E, Ward MD, Weber F, Yellowlees LJ (1994) *J Chem Soc Dalton Trans* 799
- Barthram AM, Ward MD (2000) *New J Chem* 24:501
- Barthram AM, Cleary RL, Kowallick R, Ward MD (1998) *Chem Commun* 2695
- García-Cañadas J, Meacham AP, Peter LM, Ward MD (2003) *Angew Chem Int Ed* 42:3011
- García-Cañadas J, Meacham AP, Peter LM, Ward MD (2003) *Electrochem Comm* 5:416
- Schwab PFH, Diegoli S, Biancardo M, Bigozzi CA (2003) *Inorg Chem* 42:6613
- Biancardo M, Schwab PFH, Bigozzi CA (2003) *Coll Czech Chem Comm* 68:1710
- Meacham AP, Wijayantha KGU, Peter LM, Ward MD (2004) *Inorg Chem Comm* 7:65
- Cleland WE Jr, Barhhardt KM, Yamanouchi K, Collison D, Mabbs FE, Ortega RB, Enemark JH (1987) *Inorg Chem* 26:1017
- Ung VA, Bardwell DA, Jeffery JC, Maher JP, McCleverty JA, Ward MD, Williamson A (1996) *Inorg Chem* 35:5290
- Harden NC, Humphrey ER, Jeffery JC, Lee S-M, Marcaccio M, McCleverty JA, Rees LH, Ward MD (1999) *J Chem Soc Dalton Trans* 2417
- Bayly SR, Humphrey ER, de Chair H, Paredes CG, Bell ZR, Jeffery JC, McCleverty JA, Ward MD, Totti F, Gatteschi D, Courric S, Steele BR, Screttas CG (2001) *J Chem Soc Dalton Trans* 1401
- McDonagh AM, Bayly SR, Riley DJ, Ward MD, McCleverty JA, Cowin MA, Morgan CN, Varrazza R, Pentyl RV, White IH (2000) *Chem Mater* 12:2523
- McCleverty JA, Ward MD (2003) Nitrosyl and oxo complexes of molybdenum. In: Lever ABP (ed) *Comprehensive coordination chemistry*, 2nd ed, vol. 2. Elsevier, Oxford, pp 743–757
- Creutz C, Taube H (1973) *J Am Chem Soc* 95:1086
- Ward MD (1995) *Chem Soc Rev* 24:121
- Qi Y, Desjardins P, Wang ZY (2002) *J Opt A Pure Appl Opt* 4:S273
- Qi YH, Desjardins P, Wang ZY (2002) *Opt Mater* 21:255
- Qi Y, Zhi ZY (2003) *Macromolecules* 36:3146
- Biancardo M, Schwab PFH, Argazzi R, Bigozzi CA (2003) *Inorg Chem* 42:3966
- Müller-Westerhof UT, Vance B (1987) Dithiolenes and related species. In: Wilkinson G, Gillard RD, McCleverty JA (eds) *Comprehensive coordination chemistry*, 1st edn, vol. 2. Pergamon, Oxford, pp 595–631
- Müller-Westerhof UT, Vance B, Yoon DI (1991) *Tetrahedron* 47:909
- Aragoni MC, Arca M, Demartin F, Devillanova FA, Garau A, Isaia F, Lelj F, Lippolis V, Verani G (1999) *J Am Chem Soc* 121:7098
- Bigoli F, Cassoux P, Deplano P, Mercuri ML, Pellinghelli MA, Pintus G, Serpe A, Trogu EF (2000) *J Chem Soc Dalton Trans* 4639
- Aragoni MC, Arca M, Cassano T, Denotti C, Devillanova FA, Isaia F, Lippolis V, Natali D, Nitti L, Sampietro M, Tommasi R, Verani G (2002) *Inorg Chem Commun* 5:869
- Vickers SJ, Ward MD (2005) *Electrochem Commun* 7:389