Dinuclear Complexes Containing Ferrocenyl and Oxomolybdenum(V) Groups Linked by Conjugated Bridges: A New Class of Electrochromic Near-Infrared Dye

Siu-Ming Lee, Massimo Marcaccio, Jon A. McCleverty,* and Michael D. Ward*

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

Compounds which absorb light strongly in the near-infrared (NIR) region of the spectrum are of intense interest because of their potential use in optical data storage devices in which reading and writing is performed by diode lasers which operate in this region of the spectrum.[1] Examples of such compounds include metal dithiolene complexes,[2] highly conjugated quinones,[3] and phthalocyanines.[1,4] If the strong NIR absorption is not permanent but may be switched on by some external perturbation, then the compound is a NIR "color former" which is of additional interest in the areas of optoelectronics and switchable electrochromic dyes.[5] Such compounds are relatively rare.

We describe here two complexes (**1** and **2**, Scheme 1), each containing a ferrocenyl group attached via a conjugated spacer to an oxo-Mo(V) fragment, which develop a very strong NIR absorption following oxidation of both termini and are therefore switchable NIR dyes. We became interested in these compounds because their donor-conjugated bridge-acceptor construction could be appropriate for nonlinear optical applications[6] and have also found that they have remarkable optical properties which are reported here.

The complexes were simply prepared by reaction of the ferrocenylphenols[7,8] HL^1 and HL^2 with [Mo(O)(Tp*)-

Scheme 1

HL^1 R = H
1   R = {Mo(Tp*)(O)Cl}

HL^2 R = H
2   R = {Mo(Tp*)(O)Cl}
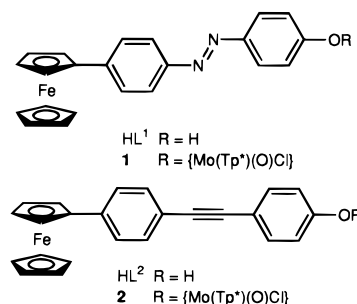
Cl$_2$] [Tp* = hydrotris(3,5-dimethylpyrazolyl)borate].[9,10] The mononuclear complex [Mo(O)(Tp*)(Cl)(OC$_6$H$_5$)] (**3**)[10b] was also examined as a spectroscopic model for the Mo fragments of **1** and **2**. Cyclic voltammetric studies (Table 1, Figure 1) show that **1** and **2** undergo three chemically reversible redox processes, at potentials consistent with known properties of the component parts: there is an Fe(II)/Fe(III) couple for the ferrocenyl fragment and both Mo(V)/Mo(VI) and Mo(V)/Mo(IV) couples for the oxomolybdenum fragment.[10a] The complexes were then subjected to a spectroelectrochemical study (Table 2).[11,12]

Initially we needed to examine the spectroelectrochemical behavior of each of the two chromophores individually, for which purpose we used the mononuclear oxo-Mo(V) complex **3** and the ferrocenyl ligand HL^2. On oxidation of **3** to [**3**]$^+$, a metal-centered oxidation of Mo(V) to Mo(VI), the main spectral change is replacement of the single phenolate-to-Mo(V) lmct band at 520 nm by two more intense bands at 681 and 475 nm, which are likely to be lmct transitions originating from the phenolate and oxo groups. The higher energy transitions are less affected by the oxidation.

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(5) (a) Yoshida, K.; Oga, N.; Kadota, M.; Ogasahara, Y.; Kubo, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 1114. (b) Kubo, Y. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2521. (c) Kubo, Y. *J. Chem. Soc., Perkin Trans. 1,* **1994**, 1787. (d) Ito, K.; Kuwabara, M.; Fukunishi, K.; Fujiwara, Y. *Dyes and Pigments* **1997**, *34*, 297.
(6) (a) Coe, B. J.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A.; Bloor, D.; Cross, G.; Axon, T. L. *J. Chem. Soc., Dalton Trans.* **1995**, 673. (b) Coe, B. J.; Foulon, J.-D.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A.; Bloor, D.; Cross, G. H.; Axon, T. L. *J. Chem. Soc., Dalton Trans.* **1994**, 3427. (c) Coe, B. J.; Jones, C. J.; McCleverty, J. A.; Bloor, D.; Cross, G. *J. Organomet. Chem.* **1994**, *464*, 225.
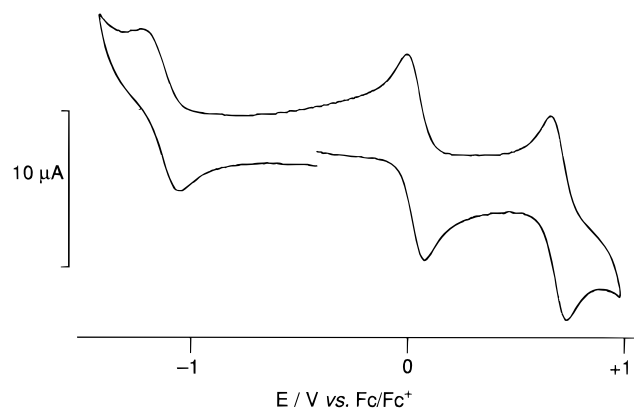(7) HL^1 was prepared by the published method (ref 6a). HL^2 was prepared by (i) converting 4-iodophenylferrocene (FcC$_6$H$_4$I) to the terminal acetylene derivative (FcC$_6$H$_4$CCH) according to standard method (ref 8) and then (ii) a Heck coupling of FcC$_6$H$_4$CCH with 4-iodophenol in Et$_2$NH catalyzed by Pd(PPh$_3$)$_2$Cl$_2$/CuI. Full details will be published later.
(8) Ames, D. E.; Bull, D.; Takundwa, C. *Synthesis* **1981**, 364.

(9) Complexes **1** and **2** were prepared by reaction of [Mo(Tp*)(O)-Cl$_2$] (0.20 g, 0.42 mmol) with HL^1 or HL^2, respectively (0.50 mmol), in toluene (20 mL) containing dry Et$_3$N (0.5 mL) at reflux under N$_2$ for 10 h. After evaporation to dryness the crude solid was purified by column chromatography (silica, 1:1 CH$_2$Cl$_2$/hexane) with the main green (**2**) or brown (**1**) band collected in each case. Yields: **1**, 18%; **2**, 40%. Satisfactory elemental analyses were obtained, and the FAB mass spectra gave an intense molecular ion peak in each case: *m/z* 827 (**1**), 823 (**2**). Complex **3** was prepared as described earlier (ref 10b).
(10) (a) Ung, V. A.; Bardwell, D. A.; Jeffery, J. C.; Maher, J. P.; McCleverty, J. A.; Ward, M. D.; Williamson, A. *Inorg. Chem.* **1996**, *35*, 5290. (b) Cleland, W. E., Jr.; Barkhart, K. M.; Yamanouchi, K.; Collison, D.; Mabbs, F. E.; Ortega, R. B.; Enemark, J. H. *Inorg. Chem.* **1987**, *26*, 1017.
(11) UV/vis spectroelectrochemical studies were carried out in a homemade OTTLE (optically transparent thin layer electrode) cell, built according to the design of Yellowlees et al. (ref 12). The cuvette path length was 0.4 mm. The working electrode was a Pt/Rh (90:10) gauze with an optical transparency of about 40%, the auxiliary electrode was a thick Pt wire, and the reference electrode was Ag/AgCl. The cell was mounted in the sample compartment of a Perkin-Elmer Lambda 19 spectrophotometer. The potentials were applied using an Amel model 552 potentiostat connected to an Amel model 566 function generator, and spectra were recorded periodically until electrolysis was complete (typically 30–60 min). All experiments were carried out at −30(±1) °C. Reversibility was checked by reversing the electrolysis and ensuring that the spectrum of the starting material was exactly regenerated.
(12) MacGregor, S. A.; McInnes, E.; Sorbie, R. J.; Yellowlees, L. J. in *Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds;* Pombiero, A. J. L., McCleverty, J. A., Eds.; NATO ASI Series; Kluwer Academic Press: Dordrecht, The Netherlands, 1993; Vol. C385, p 503.

Table 1. Electrochemical Data for the New Complexes[a]

complex	Fe(II)/Fe(III)	Mo(IV)/Mo(V)	Mo(V)/Mo(VI)
1	+0.03 (80)	−1.08 (120)	+0.76 (80)
2	+0.03 (80)	−1.11 (140)	+0.69 (90)
3[b]		−1.21 (200)	+0.68 (90)

[a] All measurements made in CH_2Cl_2, containing 0.1−0.2 M $^nBu_4PF_6$ as base electrolyte. Potentials are in volts vs the ferrocene/ferrocenium couple, and peak−peak separations (in mV) are in parentheses. All processes are chemically reversible. [b] From ref 10a.
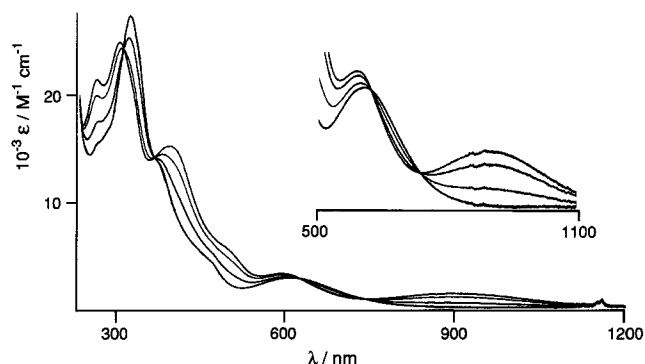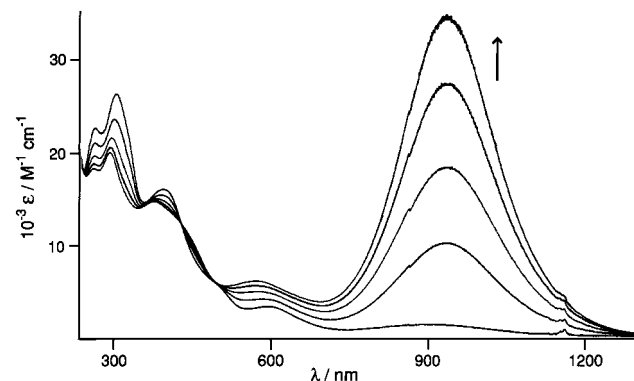

Figure 1. Cyclic voltammogram of **2** in CH_2Cl_2 (scan rate 0.2 V s^{-1}).

Figure 2. Electronic spectra recorded during oxidation of **2** to $[2]^+$ at 243 K in CH_2Cl_2.

Figure 3. Electronic spectra recorded during oxidation of $[2]^+$ to $[2]^{2+}$ at 243 K in CH_2Cl_2.

Reduction of [**3**] to [**3**]$^-$ [reduction of Mo(V) to Mo(IV)] showed little of interest beyond the disappearance of the phenolate-to-Mo(V) lmct band at 520 nm.

In neutral HL^2 the transitions at 450 nm and ca. 365 nm are mlct transitions characteristic of substituted ferrocenes.[13] The intense transition at 316 nm is obviously ligand-centered, its relatively low energy being a consequence of the extended conjugated system provided by the substituent. On oxidation to $[HL^2]^+$, none of these three transitions changes significantly in energy, although the intensities of the former two approximately double. A new transition appears at 860 nm, which is characteristic of ferrocenium derivatives and is an lmct transition that has become possible because of the hole in the metal-based e_{2g} level.[14]

Knowing the spectroscopic behavior of the component chromophores, the spectroelectrochemical properties of **1** and **2** were then examined at 243 K in CH_2Cl_2. In each case the first oxidation (ferrocene to ferrocenium) results in the appearance of the ferrocenium lmct transition[14] at about 900 nm (Figure 2). At the same time the phenolate-to-Mo(V) lmct band at ca. 600 nm is blue-shifted, consistent with the phenolate-based HOMO being lowered in energy as a result of conjugation with a positive charge. The remaining transitions are also identifiable as being associated with one or other of the component parts with some minor perturbations (Table 2), and it is clear that the first oxidation is essentially localized on the ferrocene fragment.

After the second (Mo-based) oxidation of these complexes, such that they now contain both ferrocenium and oxo-Mo(VI) fragments, a dramatic change occurs at the low-energy end of the electronic spectra: an intense new transition appears which dominates the spectrum and is both much stronger and at lower energy than the 681 nm lmct transition that appeared on oxidation of **3**. This occurs at 860 nm ($\epsilon = 20\,000$ dm^3 mol^{-1} cm^{-1}) for $[1]^{2+}$; and 936 nm ($\epsilon = 34\,000$ dm^3 mol^{-1} cm^{-1}) for $[2]^{2+}$ (Figure 3) and therefore obscures the much weaker ferrocenium-centered lmct. Given that this transition only appears when *both* metal termini are oxidized, it cannot be a metal-to-metal charge transfer between electron-rich and electron-poor termini. We suggest that the double oxidation imparts a planar, quinonoidal character to the conjugated bridging group (Figure 4), thereby introducing a new low-energy, fully allowed $\pi \rightarrow \pi^*$ transition delocalized over the bridging fragment; such transitions are characteristic of extended quinones.[3] This implies that the two formally metal-centered oxidations have some ligand-centered character. For oxo-Mo(V) complexes of this type with phenolate ligands, we have shown that oxidation to (formally) Mo(VI) has a significant degree of ligand-based character;[10a] also, addition of highly conjugated substituents to ferrocenyl cores results in a substantial degree of mixing of metal and ligand orbitals.[13]

A few significant points are as follows. First, the intensity of these NIR transitions is comparable with those of compounds that have found practical applications in prototypical data-storage devices.[1] Second, the first oxidation does not on its own become delocalized over the bridging group, but remains ferrocenium-localized (Figure 1) until the second oxidation has occurred. In consequence, a one-electron reduction of the dication to the monocation is sufficient to switch off

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Table 2. Results of UV/vis Spectroelectrochemical Studies (CH₂Cl₂, 243 K)

compd	λ_{max}/nm [10^{-3} ϵ/M^{-1} cm^{-1}]					
1		650 (sh)[a]	490 (12)[b]	386 (28)[c]		250 (sh)
2		597 (2.7)[a]	470 (sh)[b]	373 (sh)[c]	318 (27)	
3		520 (1.8)[a]		340 (6.2)[c]		266 (9.8)
HL²			451 (1.5)[b]	365 (sh)[c]	316 (44)	
[1]⁺	867 (1.7)[d]	640 (sh)[a]	500 (sh)[b]	398 (27)[c]	295 (18)	253 (27)
[2]⁺	902 (1.3)[d]	591 (3.2)[a]	500 (sh)[b]	391 (14)[c]	301 (24)	260 (21)
[HL²]⁺	860 (0.8)[d]		447 (4.0)[b]	365 (sh)[c]	316 (43)	
[1]²⁺	860 (20)[e]	580 (sh)[f]		388 (20)[c]	298 (18)	246 (sh)
[2]²⁺	936 (34)[e]	568 (5.5)[f]		373 (13)[c]	289 (18)	257 (17)
[3]⁺	681 (12)[f]	475 (5.4)[f]		359 (6.8)[c]		

The following assignments are reasonable: [a]phenolate→Mo(V) lmct. [b]Lower energy ferrocenyl-based transition. [c] Cl(π) → Mo(V) lmct and/or the higher energy ferrocenyl-based transition. [d] Ferrocenium-based lmct (Figure 2). [e] $\pi \rightarrow \pi^*$ transition associated with quinonoidal form of bridging group (Figures 3 and 4). [f] lmct involving Mo(VI).
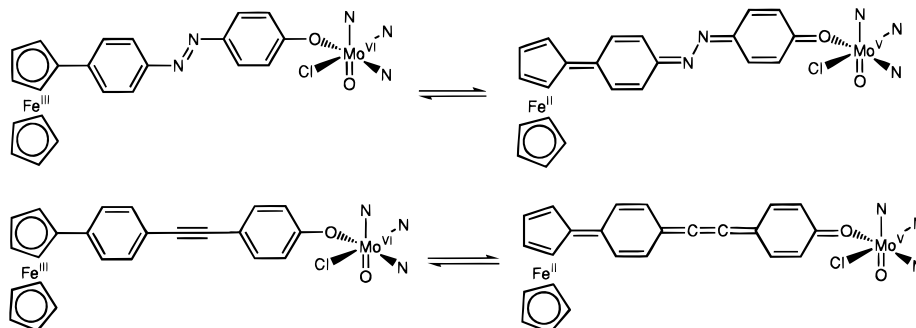
Figure 4. Quinonoidal character of the bridging group in the doubly oxidized complexes **[1]**²⁺ and **[2]**²⁺.

the NIR transition completely. Third, although quite-oxidizing potentials are necessary to effect the second (Mo-centered) oxidation, replacement of the chloride ligand by better electron-donors such as methoxide will make this oxidation much easier and therefore allow the electrochromic switching effect to occur under relatively mild conditions.[10b]