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Redox-Functionalised Terpyridines. Ferrocenylhydroxyethyl and Ferrocenylvinyl Groups Covalently Attached to 2,2':6',2"-terpyridine. Oxidative Electropolymerisation of the Vinyl Derivative and its Metal Complexes.

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Abstract: The reaction of 4'-methyl-2,2':6',2"-terpyridine with ferrocenecarbaldehyde in the presence of lithium di-isopropyl-amide allowed us to isolate the ferrocene-functionalised terpyridine derivative 4'-[2-ferrocenyl-2-hydroxyethyl]-2,2':6',2"-terpyridine (L_1) in a 80 % yield. Dehydration of L_1 with pyridinium toluene-p-sulphonate yielded the corresponding ferrocenylvinyl derivative 4'-ferrocenylvinyl-2,2':6',2"-terpyridine, (L_2). Their spectroscopic and electrochemical characterisation and the synthesis of homoleptic complexes of L_1 and L_2 in acetonitrile has been carried out. The oxidative electropolymerisation of L_2 and the enhancement or inhibition of the polymerisation process due to the presence of different transition metal ions is also reported. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Supramolecular systems containing a number of electronically coupled photo- or redox-active centres are of considerable current interest.[1-3] Interest in oligopyridines has grown rapidly in recent years due to their ability of forming transition metal complexes which have been used as both redox- and photo-active building blocks in molecular and supramolecular chemistry.[4-6] Special attention has been focused upon the synthesis of multicomponent systems exhibiting intermetallic energy- or electron-transfer processes. On the other hand the ferrocene group has been widely used as redox-active fragment in molecular systems due to its redox properties, remarkable stability and its well known chemistry;[7] additionally, due to its facility to be oxidised, ferrocene is expected to act as electron donor in these systems. However not many studies have been published in which ferrocene and oligopyridines are covalently linked.[2,8-9] This can be of importance since electron-transfer processes can be facilitated in systems coupled covalently.[10] We shall thus report on the preparation, characterisation and electrochemical properties of novel molecules containing ferrocenylhydroxyethyl and ferrocenylvinyl electron-transfer donor moieties covalently anchored to a 2,2':6',2"-terpyridine.

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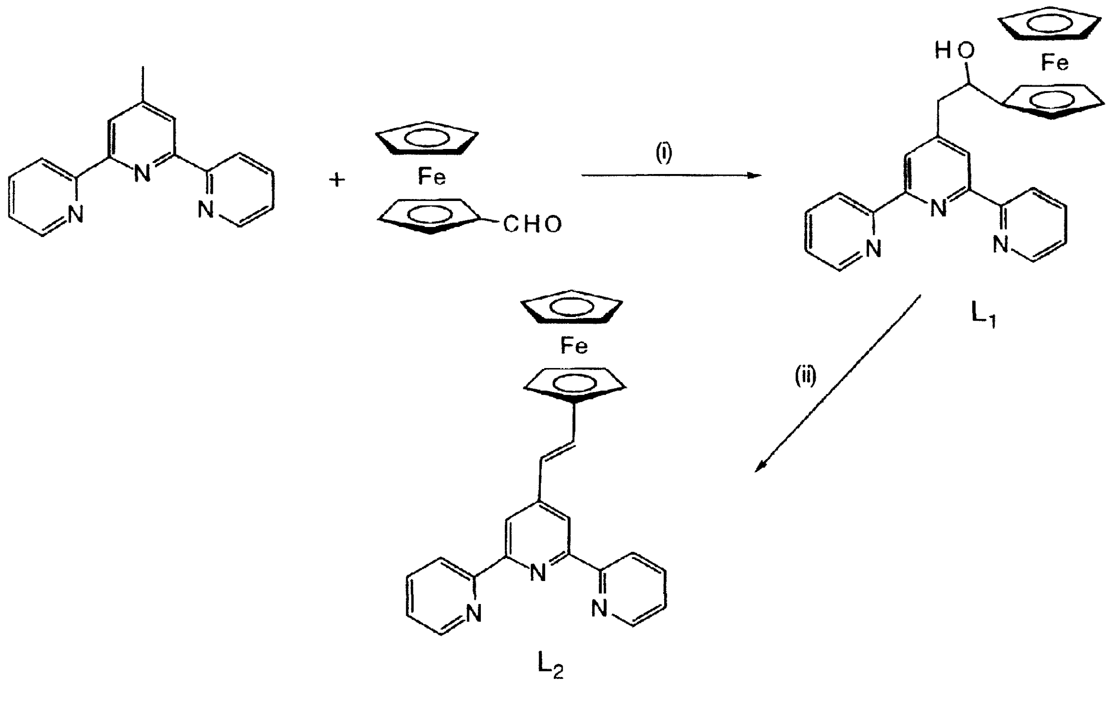
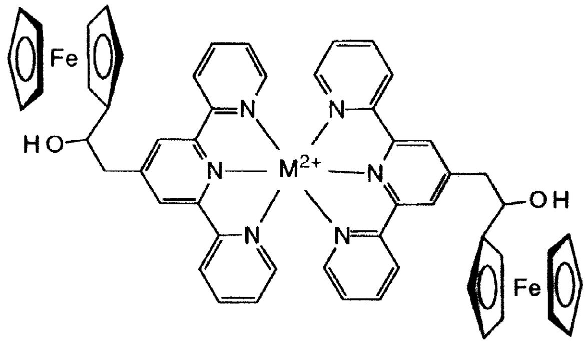
RESULTS AND DISCUSSION

Lithiation of 4'-methyl-2,2':6',2"-terpyridine using freshly prepared lithium di-isopropyl-amide (LDA) in tetrahydrofuran at low temperature and further addition of ferrocenecarbaldehyde gave the product 4'-[2-ferrocenyl-2-hydroxyethyl]-2,2':6',2"-terpyridine, (L_1) in a 80 % yield. The ^1H NMR spectrum of L_1 is characteristic. The ferrocenyl group shows a group of three resonances; a five proton singlet for the unsubstituted cyclopentadienyl ring and two apparent triplets corresponding to protons α and β in the monosubstituted ring. The five groups of signals at low field (δ 7.31 to 8.72) are as expected for a 4'-substituted terpyridine. The spectrum is completed by signals for the CH_2 and CH protons and a high field resonance at δ 2.1 attributed to the OH group. The treatment of L_1 with pyridinium-4-toluene sulfonate and further column chromatography gave an unidentified violet product and the corresponding dehydrated molecule L_2 in 25 % yield (see Scheme 1). It is noteworthy that only the trans isomer was isolated as previously reported in similar reactions involving the attachment of ferrocenyl groups to methyl-2,2'-bipyridine derivatives.[11] Apart from the two doublets for the vinyl protons the ^1H NMR spectrum of L_2 displays the expected characteristic signals for the ferrocenyl and the 4'-substituted terpyridine groups. The FAB mass spectra, IR and analytical data for L_1 and L_2 are also in agreement with the proposed formulation.



Scheme 1.- *(i)* lithium di-isopropyl-amide; *(ii)* pyridinium-4-toluene sulfonate.

L_1 and L_2 can be used as building blocks for the development of supramolecular arrays. Multicomponent systems can be easily prepared by reaction of L_1 or L_2 with transition metal ions to produce the corresponding homoleptic complexes $[M(L)_2]^{2+}$ (see Figure 2).



Scheme 2.- Homoleptic complex with L_1.

We have carried out electrochemical studies to evaluate the effect that the presence of the ferrocenyl groups have on the central metal ion and the effect that the central M-tpy core (tpy = terpyridine group) could have on the peripheral redox-active groups. Electrochemical studies were performed in acetonitrile at 25 °C using tetrabutylammonium perchlorate as supporting electrolyte. Table 1 shows the oxidation potential of L_1, L_2 and their homoleptic $[M(L)_2]^{2+}$ complexes ($L = L_1, L_2$; $M^{2+} = Fe^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}$) which were prepared *in situ* by addition of the corresponding amount of the appropriate metal salt.

Table 1 Electrochemical Data.

Compound	M^{II}-M^{III}	$Fc\text{-}Fc^+$	Half-peak width
ferrocene		390[a,b]	90[c]
L_1		380	90
L_2		450	90
$[Fe(L_1)_2][ClO_4]_2$	1080[a]	395	120
$[Co(L_1)_2][NO_3]_2$	280	400	
$[Zn(L_1)_2][NO_3]_2$		395	110
$[Cd(L_1)_2][NO_3]_2$		395	120
$[Co(L_2)_2][NO_3]_2$	240	533[d]	125
$[Zn(L_2)_2][NO_3]_2$		505[d]	130
$[Cd(L_2)_2][NO_3]_2$		488[d]	120

[a]Determined as half wave potential $E_{1/2}$ from rde. [b]Ferrocene to ferrocenium oxidation potential. [c] From differential pulse voltammetry. [d] Sweeping range 0 to +0.8 V.

When comparing receptors L_1 and L_2 with ferrocene, a shift to more cathodic potentials for L_1 and to more anodic potentials for L_2 can be observed in accordance with the donating nature of the alcohol linkage and the withdrawing nature of the olefinic bound. On the other hand the effect that the presence of the oxidised ferrocenium groups have on the central core can be evaluated by comparison to the oxidation potential of the Fe^{2+}-tpy core in $[Fe(Me\text{-}tpy)_2]^{2+}$ (1030 mV), and in the complex $[Fe(L_1)_2]^{2+}$ (1080 mV). This anodic shift of the oxidation potential of the central iron atom Fe^{2+} in $[Fe(L_1)_2]^{2+}$ when compared with $[Fe(Me\text{-}tpy)_2]^{2+}$ points out the effect of the charge built-up after oxidation of the two ferrocenyl groups. Half-peak width (from differential pulse voltammetry) of L_1 and L_2 has been found to be 90 mV, a value close to that found for ferrocene. However in homoleptic complexes half-peak width was near 120 mV. As reported previously 90 mV half-peak width is expected for a *n*-electron process in a redox system containing *n* non-interfering redox sites. A half-peak width of 120 indicates that comproportionation constant of the equilibrium in equation (1) (Fc = ferrocenyl group) is $K_c = 9.35$.[12]

$$[Fc^{o}\text{-}Fc^{o}] + [Fc^{+}\text{-}Fc^{+}] \rightleftharpoons [Fc^{o}\text{-}Fc^{+}] \qquad (1)$$

This results appear to indicate that although the mixed-valence species are basically not stabilised there must be some through-bond or more likely some through-space path of interaction between the two ferrocenyl centres in the $[M(L)_2]^{2+}$ complex which only exist when two L_1 or L_2 molecules are linked by a central atom.

Additionally we have observed an interesting behaviour in the electrochemical response of L_2. Oxidative scanning showed an oxidation process at + 0.49 V *versus* SCE and when the scanning is reversed the corresponding reduction process for the reversible ferrocene/ferricinium couple was found (see Table 1). However when the oxidative scanning is extended to more anodic potentials a new and unexpected reversible oxidation wave was observed at + 1.1 V, whereas the reversibility of the ferrocene couple was lost. Upon continuous potential cycling intensity of the new peak increases, whereas that of ferrocene disappears indicating that the electropolymerisation process occurs (see Figure 1). Modified electrodes with polymeric films when transferred to clean CH_3CN (0.1 mol dm^{-3} tetrabutylammonium perchlorate) were stable and repetitive scan in the anodic region did not result in the decrease of the + 1.1 V voltammetric wave. Similar results were found in other solvents such as CH_2Cl_2 and water, even after the treatment of the polymeric film with acid. This behaviour is in contrast with that of L_1 or similar related ligands such as 4'-vinyl-2,2':6',2''-terpyridine, for which no electropolymerisation was observed neither by oxidative or reductive scanning. Coating of electrode surfaces with thin stable mono or multilayer films of metallic complexes is of great interest for diverse technical applications. Transition metal complex polymer modified electrodes have been mainly obtained from polypyridine ligand complexes, with vinyl-substituted bipyridine ligands being the most extensively studied for preparing modified surfaces by reductive electropolymerisation techniques.[13] Polymer films formed by oxidative electropolymerisation of N-alkylpyrroles,[14] or aniline-substituted bipyridine[15] ligands have also been described. However relatively less effort has been devoted to electropolymerisation using larger polypyridine receptors such as terpyridines.[16]

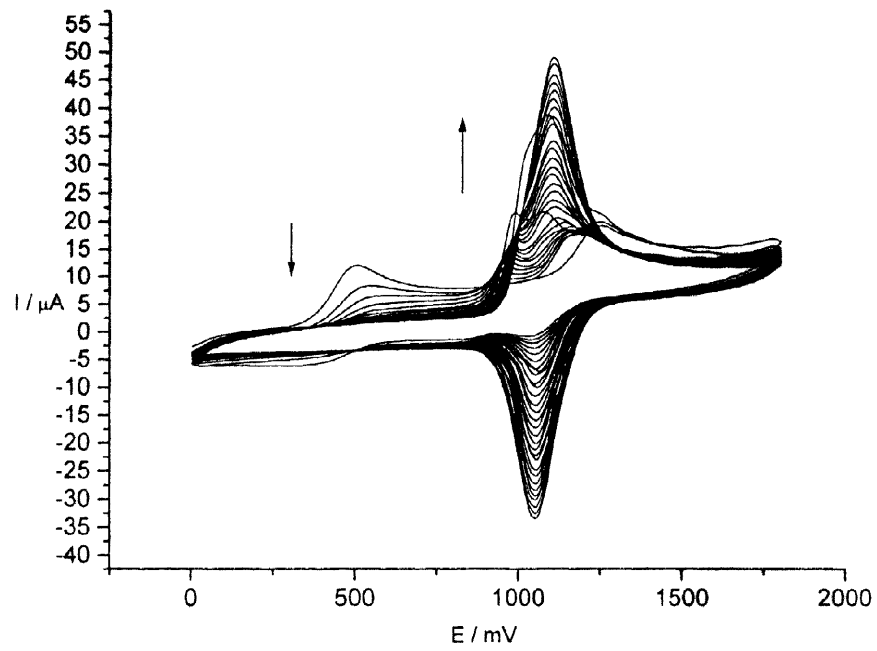


Figure 1.- Thirty sequential cyclic voltammograms of a solution containing L_2 (7 x 10^{-4} mol dm^{-3}) in CH_3CN, 0.1 mol dm^{-3}, tetrabutylammonium perchlorate.

In considering the electropolymerisation of L_2 it is necessary to be aware of the nature of the transformations involved. The final +1.1 V redox couple found in the polymer is attributed to the existence of a Fe^{II}/Fe^{III} couple in a terpyridine environment. In fact the homoleptic $[Fe(L_1)_2]^{2+}$ complex shows a similar oxidation potential for the metal-terpyridine core. Despite the ferricinium group appear to be stable within the cyclic voltammetry time-scale, the high potential applied in the working electrode, the presence of a positive charge in the ferricinium group and its proximity to the vinyl moieties, probably induces the oxidative electropolymerisation of the vinyl or vinyl-cyclopentadienyl backbone to occur and further rupture of the ferrocenyl groups and reorganisation to produce Fe^{II} in a terpyridine environment.

The addition of different metal ions to a solution of L_2 can enhance or inhibit the polymerisation process. That is to the best of our knowledge quite unusual, taking into account that polymerisation is usually dependent on the nature of the complex being electropolymerised and only a chemical modification (for example by including more vinyl groups) can enhance polymerisation rate. Addition of Fe^{2+} to give the homoleptic $[Fe(L_2)_2]^{2+}$ complex enhance the electropolymerisation process. $[Fe(L_2)_2]^{2+}$ shows a very similar electrochemical behaviour of that observed for the free L_2 receptor, and with continuous cycling the wave at + 1.1 V increases in peak current whereas the ferrocene/ferricinium wave at + 0.52 V disappears. Additionally when the modified electrode is transferred to clean CH_3CN a similar polymeric film, from the electrochemical viewpoint to that obtained for L_2 was found. Electropolymerisation of the $[Fe(L_2)_2]^{2+}$ complex is faster than polymerisation of the free L_2 ligand as can be observed in Figure 2 where the intensity of the +1.1 V peak is plotted as a function of the number of scans. In contrast addition to a solution of L_2 of metal such as Co, Cd or Zn to produce the corresponding homoleptic complexes inhibit the electropolymerisation process of L_2 and only the reversible ferrocene/ferricinium couple is found. The $[Co(L_2)_2]^{2+}$ complex also shows the metal-based Co^{II}/Co^{III} oxidation process at + 0.24 V.

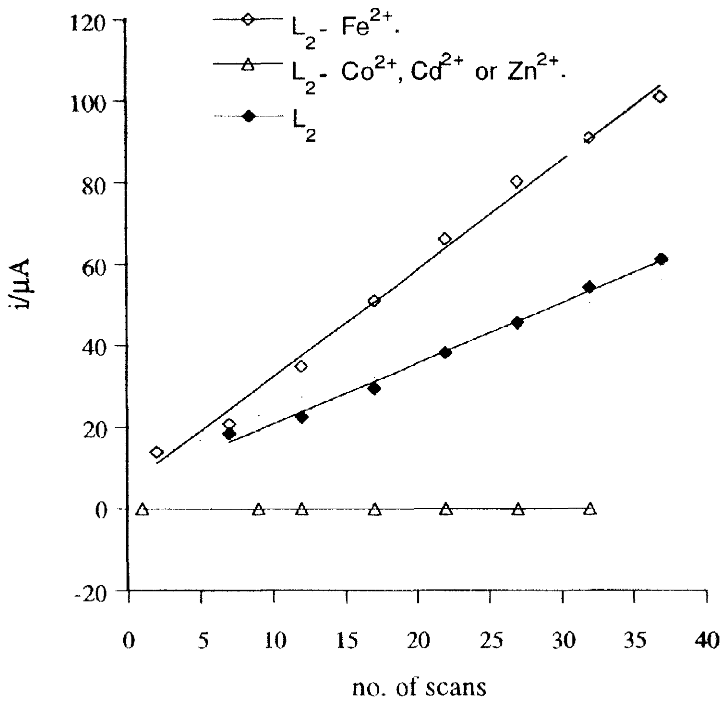


Figure 2.- Plot of $i_{p,oxd}$ for the + 1.1 V wave versus the number of cyclic scans for L_2 and L_2 in the presence of Fe^{2+}, Co^{2+}, Cd^{2+} or Zn^{2+}.

ACKNOWLEDGEMENTS

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EXPERIMENTAL

General

^{1}H NMR spectra were recorded with a Varian Gemini spectrometer using TMS as reference. Infrared spectra were recorded as KBr pellets on Perkin-Elmer 1750 spectrometer. Electrochemical measurement were performed using a potentiostat galvanostat type PJT 120-1 with a programmable Tacussel IMT-1 connected to a potentiostat Tacussel PJT 120-1. A conventional three-electrode configuration, with graphite as working electrode, platinum wire as auxiliary electrode and saturated calomel electrode (SCE) as reference. Acetonitrile freshly destilled, was used as solvent in the electrochemical experiments. The base electrolyte was 0.1 mol dm^{-3} of tetrabutylammonium perchlorate. 4'-methyl-2.2':6',2"-terpyridine was prepared according to literature methods,[15] whereas ferrocenecarbaldehyde was used as supplied by Aldrich.

Synthesis of *4'-[2-ferrocenyl-2-hydroxyethyl-2,2':6',2"-terpyridine*, (L_1). A three-necked flask (500 mL) equipped with magnetic stirrer, thermometer, pressure equalising dropping funnel, and side arm connected to nitrogen, was charged with di-isopropylamine (0.607 g, 6 mmol) and dry, freshly destilled THF (20 mL). The solution was cooled to about -75 °C with an acetone-solid CO_2 bath, and n-BuLi (6.2 mmol) in hexane was added. After stirring for a while, 4'-methyl-2,2':6',2"-terpyridine (1.24 g, 5 mmol) previously dissolved in dry THF (40 mL) was added via a dropping funnel to produce a intense blue solution. After 30 minutes of stirring at -78°C and 2 hours at 0°C, ferrocencarbaldehyde (1.025 g, 4.8 mmol) in 20 mL of THF were added and the mixture was stirred overnight. The mixture was quenched with methanol (5mL), poured into water, and extracted three times (50 mL) with CH_2Cl_2. The extracts were combined, dried over $MgSO_4$ anhydrous, and the solvent removed in vacuo. The residue was chromatographied on silica gel using CH_2Cl_2-CH_3OH (99:1) as eluent giving a dark oil, which crystallised when adding diethyl ether to give L_1.(Found: C, 66.3; H, 5.0; N, 8.8. Calculated for $C_{27}H_{23}FeN_3O.H_2O$ requires C, 67.0 H, 5.2; N, 8.8 %). Infrared spectrum (KBr disk): 3250s, 1550m, 1530m, 1460s, 1300m, 1220m, 1200s, 1025w, 1090s, 1010w, 970s, 750s cm^{-1}. NMR ($CDCl_3$): ^1H δ 2.1 (s, 1H, COH), 3.12 (d 2H, CH_2), 4.18-4.32 (m, 9H, $C_{10}H_9$), 4.8 (m, 1H, CHOH), 7.31-7.35 [m, 2H, tpy H(5,5")], 7.83-7.89 [m, 2H, tpy H (4,4")], 8.35 [s, 2H, tpy H(3',5')], 8.61-8.64 [m, 2H, tpy H(3,3")], 8.69-8.72 [m, 2H, tpy H(6,6")]. Mass spectrum: M/z (relative intensity) 461(10), 396(10), 378(10), 367(10), 302(40), 247(100), 214(50), 186(30), 121(20).

Synthesis of *4'-ferrocenylvinyl-2,2':6',2"-terpyridine*, (L_2). A mixture of L_1 (0.461 g, 1.0 mmol), pyridinium-4-toluene sulfonate (0.251 g, 1.2 mol) and dry toluene (150 mL) was heated to reflux and water was removed with a Dean Stark trap for 4h. The reaction mixture was cooled down to room temperature and the toluene removed in vacuo. The residue was dissolved in CH_2Cl_2, washed with water and dried ($MgSO_4$). The residue was column chromatographed on alumina using CH_2Cl_2-CH_3OH (99:1) as eluent to give a brown oil, which after adding ether precipitated giving L_2. (Found: C, 68.8; H, 5.0; N, 9.0 Calculated for $C_{27}H_{21}FeN_3.H_2O$ requires C, 69.3 H, 5.0; N, 9.1 %). Infrared spectrum (KBr disk): 1550s, 1450s, 1380s, 1100s, 780s cm^{-1}. NMR ($CDCl_3$): ^1H δ 4.16 (t, 5H, C_5H_5), 4.35 (d, 2H, C_5H_4), 4.53 (d, 2H, C_5H_4), 6.8-6.9 (d, 1H, =CH), 7.33-7.36 [m, 2H, tpy H(5,5")], 7.39-7.45 (d, 1H, =CH-), 7.87-7.90 [m, 2H, tpy H(4,4")], 8.47[s, 2H, tpy H(3',5')], 8.63-8.66 [m, 2H, tpy H(3,3")], 8.73-8.75 [m, 2H, tpy H(6,6")]. Mass spectrum: M/z (relative intensity) 443(50), 378(80), 302(10), 188(20), 149(50), 71(100).

Homoleptic complexes of L_1 and L_2 were prepared *in situ* for the electrochemical experiments but were not isolated. They were generated by adding to an acetonitrile solution of the ligand the stoichiometric amount (ligand-to-metal ratio 2:1) of the appropriate metal salt (iron(II) perchlorate, cobalt(II) nitrate, cadmium(II) nitrate or zinc(II) nitrate) dissolved in acetonitrile. This produces solutions of the corresponding $[M(L)_2]^{2+}$ complexes.

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