ELECTROCHROMIC BEHAVIOUR OF POLYNUCLEAR RUTHENIUM COMPLEXES ON NANOCRYSTALLINE SnO$_2$

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Dedicated to Professor Sergio Roffia in recognition of his achievements.

The trinuclear [{Ru(NH$_3$)$_4$(py-COOH)}(μ-CN){Ru(bpy)$_2$}(μ-CN){Ru(NH$_3$)$_4$(py-COOH)}]$^{6+}$ (py-COOH = isonicotinic acid, bpy = 2,2′-bipyridine) (**1**) and dinuclear [{Ru(dcb)$_2$}$_2$L]$^{7-}$ (dcb = 2,2′-bipyridine-4,4′-dicarboxylic acid, H$_3$L = 9-phenyl-2,3,7-trihydroxy-6-fluorone) (**2**) complexes were prepared and their spectroelectrochemical behaviour characterised in solution and on conductive glass electrodes layered with Sb-doped nanocrystalline SnO$_2$. The systems display a reversible redox response in a narrow potential range (–0.5 to +0.5 V *vs* SCE) and offer the possibility of controlling colour changes of electrochromic devices through variations of the coordinated and bridging ligands at the metal centres. SnO$_2$(Sb) electrodes loaded with these dyes show switching times of the order of ms.

Keywords: Mixed-valence compounds; Polynuclear ruthenium complexes; Electrochromic behaviour; Electrochemistry.

The chemistry and spectroscopy of mixed-valence (M-V) compounds have been object of intense investigation in the past three decades[1]. Among the various interesting aspects involved in the chemistry of mixed-valence compounds, particular attention has been paid to the study of optical electron transfer processes between weakly coupled metal centres, which are related by the Hush theory[2] to the kinetics and thermodynamic factors governing the corresponding thermal electron transfer processes. The majority of the studies in this area were carried out on dinuclear M-V compounds; only in a few cases oligomeric systems of higher nuclearity were investigated.

About 15 years ago we had a great pleasure to collaborate with the group headed by Prof. S. Roffia on a research project aimed at the elucidation of electronic interaction in multinuclear metal complexes[3,4]. The molecular systems under investigation were of the general formula given in Chart 1.
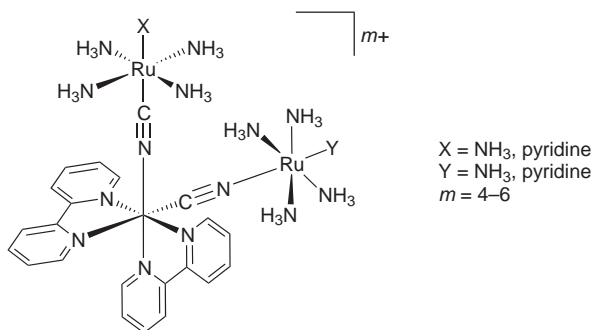
CHART 1

They were found to exhibit multisite electronic interactions, giving rise to optical electron transfer between adjacent as well as remote metal centres. In fact, several metal-to-ligand charge transfer (MLCT) and metal-to-metal charge transfer (MMCT, or IT) absorption bands corresponding to electronic transitions between different redox sites, were observed, including:

1. Ru^{II}-to-bpy MLCT originating in the Ru atom of the $\{Ru(bpy)_2\}^{2+}$ moiety (bpy = 2,2′-bipyridine);

2. Ru^{II}-to-bpy MLCT originating in the Ru atoms of the Ru-amine moieties;

3. Ru^{II}-to-Ru^{III} IT between cyano-bridged adjacent ruthenium atoms;

4. Ru^{II}-to-Ru^{III} IT between remote ruthenium atoms of the Ru-amine units.

The assignment of all these transitions was largely based on the results of the electrochemical study performed by the Roffia's group[5] and were later confirmed by resonance Raman studies[6].

The extremely rich spectra observed for this type of M-V complexes were at the basis of the recent idea of developing electrochromic materials based on discrete M-V complexes adsorbed on nanocrystalline semiconductors. A series of cyano-bridged dinuclear mixed-valence complexes of the general formula given in Chart 2 was therefore prepared and anchored through the carboxylic function of the coordinated isonicotinic acid (py-COOH) to
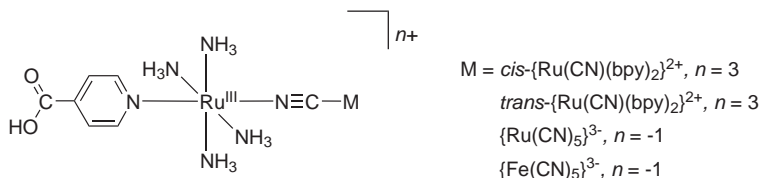

CHART 2

nanocrystalline TiO_2 or SnO_2 electrodes[7]. These complexes display a reversible electrochromic behaviour in the range of applied electrode potential ranging from –0.5 to +0.5 V *vs* SCE. Tuning of the electronic transitions in the visible and near-infrared spectral regions was achieved through changes of the solvent and of the cyano-bridged metal moiety M. This study demonstrated the flexibility of the dinuclear M-V species in modulating the transmitted light in the different spectral regions and switched our interest to more complex molecular systems that might allow for bigger colour-intensity changes between the different electronic isomers.

We wish to report herein the results of a spectroscopic study of the trinuclear species given in Chart 3 and of a dinuclear complex based on a bridging bis(dioxolene)-type ligand, given in Chart 4.
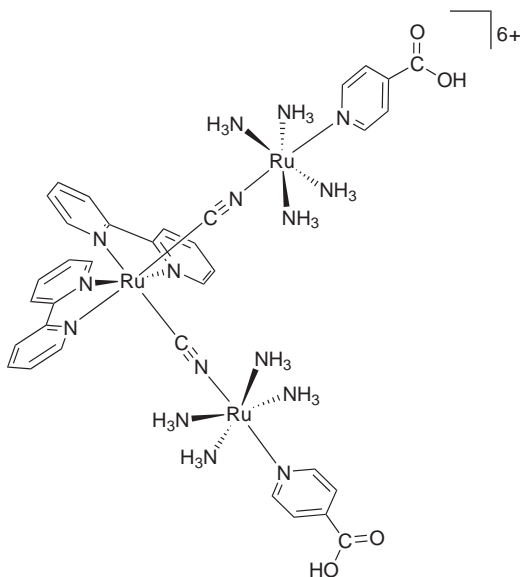

CHART 3

Because of their rich electrochemical and spectroscopic behaviour, complexes of the chelating dioxolene ligand series (dioxolene being derived from 1,2-dioxobenzene, irrespective of the oxidation state) have received a large amount of interest over the years[8–10]. With several metals, such as ruthenium and osmium, there is extensive mixing of metal- and ligand-based orbitals, making the assignment of the internal charge distribution quite challenging and a focal point of recent investigations. In the $[Ru(bipy)_2(diox)]^{n+}$ series ("diox" represents a dioxolene ligand at any oxidation state, with n = 1, 2, 3), Lever *et al.*[11] have demonstrated that ligand-
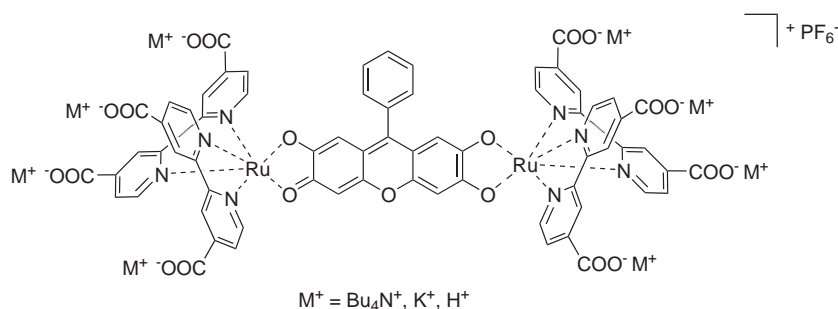
CHART 4

based redox processes between the catecholate, semiquinonate and quinone forms of diox are responsible for the different oxidation states while the metal centre remains in the +II oxidation state throughout. Due to the strong orbital mixing, the complexes display intense NIR metal-to-ligand charge transfer transitions in the Ru(II)-semiquinonate and Ru(II)-quinone forms. More recently, Ward's group has extended the work to complexes with multiple dioxolene binding sites[12,13]. The species display several well-separated and reversible redox processes accompanied by appreciable changes in the absorption spectra. For example, Barthram and Ward have recently described the preparation, electrochemical and spectroscopic properties of [[Ru(bpy)$_2$]$_2$L]$^{n+}$ (n = 1–4), where the bridging ligand is 9-phenyl-2,3,7-trihydroxy-6-fluorone (H$_3$L)[14]. The strongly electrochromic behaviour of these compounds has attracted our attention and we have attempted to transfer these properties onto the surface of a nanocrystalline inorganic semiconductor and utilise them in electrochromic devices[7,15]. Here we describe the synthesis of a related complex in which the bpy ligands have been replaced by derivatives carrying carboxyl groups for the attachment to the semiconductor surface, and its spectroelectrochemical properties both in bulk solution and anchored on an ITO glass electrode.

EXPERIMENTAL

Materials and Instrumentation

All reagents were purchased from Aldrich. The *trans*-[Ru(NH$_3$)$_4$(py-COOH]Cl (ref.[7]) (py-COOH = isonicotinic acid (ISNA)), [Ru(CN)$_2$(bpy)$_2$] (ref.[16]) (bpy = 2,2′-bipyridine) and [RuCl$_2$(dcbH$_2$)$_2$] (ref.[17]) (dcbH$_2$ = 2,2′-bipyridine-4,4′-dicarboxylic acid) complexes were prepared according to literature methods.

Transparent nanostructured films of SnO$_2$ were prepared on F-doped tin oxide (FTO) glass substrates (10 Ω/square, 0.5 μm thick, supplied by Glastron). To an aqueous dispersion of Sb-doped SnO$_2$ colloid (5 g, 15% by weight), 2 M acetic acid (2 drops) was added under stir-

ring, resulting in the immediate formation of a gel. The average particle size, as determined by transmission electron microscopy, was 5 nm. This gel was diluted with water (1.5 ml) and autoclaved at 200 °C for 12 h to yield a grey and viscous paste with a dispersion of improved particle diameters. Carbowax 20000 (0.375 g) was dissolved in the dispersion under stirring for 6–8 h. This paste was diluted with water (1 ml) in order to make it suitable for spreading on the glass substrates. Substrates were masked with a Scotch tape and the paste was evenly spread using a glass rod. After mild drying in air, the films were heated in air at 450 °C for 2 h. The resulting films were approximately 3 μm thick and the surface area factor was *ca* 1000. The films were immersed in solutions of the complexes and left overnight to complete their adsorption.

Electronic absorption spectra (300–1100 nm) were measured by using a Perkin–Elmer Lambda 40 spectrophotometer. Infrared spectra (4000–400 cm^{-1}) were collected in KBr pellets with an FTIR Bruker IFS 88S spectrometer. The electrochemical properties of the complexes were investigated with cyclic voltammetry (CV) and differential pulse voltammetry (DPV), using an Autolab PGSTAT30 apparatus and a standard three-electrode (Pt/Pt/SCE) configuration. In the CV measurements typical scan rate of 0.1 V s^{-1} was employed, while in the DPV, scan rate of 0.004 V s^{-1} and amplitude of 0.01 V were used.

Syntheses

[{Ru(NH$_3$)$_4$(py-COOH)}(μ-CN){Ru(bpy)$_2$}(μ-CN){Ru(NH$_3$)$_4$(py-COOH)}]Cl$_6$ (**1**). To a methanol solution (10 ml) containing [Ru(CN)$_2$(bpy)$_2$] (95 mg, 0.2 mmol), *trans*-[Ru(NH$_3$)$_4$-(py-COOH)]Cl (424 mg, 1 mmol) in 10^{-2} M HCl (30 ml) was added. The mixture was heated at 40 °C under argon for 30 min and a freshly prepared Zn amalgam (6 g) was added. The red solution was kept at 40 °C under argon for 5 h. After removal of the amalgam 1 M HCl (1 ml) and a few drops of 35% H$_2$O$_2$ were added, causing an immediate colour change to green-blue. After having removed methanol under reduced pressure, the reaction mixture was filtered and the solution purified by size exclusion chromatography on a 3 × 20 cm LH-20 column (Pharmacia). Elution with water gave three bands. The first band, green-blue in colour, contained the trinuclear product. The other fractions were shown to contain the dinuclear [Ru(NH$_3$)$_4$(py-COOH)(μ-NC)Ru(bpy)$_2$(CN)]$^{3+}$ species and traces of unreacted starting materials and of a [Ru(CN)$_2$(bpy)$_2$]/Zn^{2+} adduct[4]. For C$_{34}$H$_{50}$Cl$_6$N$_{16}$O$_4$Ru$_3$·2H$_2$O (1298.8) calculated: 31.44% C, 4.19% H, 17.25% N; found: 31.10% C, 4.11% H, 17.05% N.

[{Ru(dcb)$_2$}$_2$L]$^{7-}$(M$^+$)$_7$ (H$_3$L = 9-phenyl-2,3,7-trihydroxy-6-fluorone; M = K, Bu$_4$N, H) (**2**). Method *A*: Tetrabutylammonium hydroxide (0.303 mmol, 1 M in methanol) was added to a suspension of [RuCl$_2$(dcbH$_2$)$_2$] (50 mg, 0.0758 mmol) in methanol under stirring, resulting in a purple solution. After addition of Tl(OAc) (32 mg, 0.152 mmol), the mixture was heated under reflux for 12 h. The white precipitate was filtered and the red-purple solution containing [Ru{dcb(NBu$_4$)$_2$}$_2$(MeOH)$_2$] was added to a solution of 9-phenyl-2,3,7-trihydroxy-6-fluorone (12 mg, 0.0379 mmol) in DMF. The reaction mixture was heated to 60 °C for 12 h, leading to a blue colour. The hot solution was filtered off and the solvent was evaporated under vacuum. The resulting solid was dissolved in a minimum amount of water and quickly precipitated by addition of HPF$_6$ (5% in water). The precipitate was filtered and dried. For further purification, the solid was dissolved in methanol after stoichiometric treatment with tetrabutylammonium hydroxide (1 M in methanol) and chromatographed on LH 20. For C$_{195}$H$_{321}$F$_6$N$_{16}$O$_{21}$PRu$_2$ (3572.9) calculated: 65.55% C, 9.06% H, 6.27% N; found: 66.14% C, 9.32% H, 6.50% N.

MALDI-TOF, m/z: 1497 ([M$^+$]; all carboxylate groups protonated; cluster fits calculated pattern).

Method B: [RuCl$_2$(dcbH$_2$)$_2$] (50 mg, 0.0757 mmol) was suspended in methanol under stirring and a solution of 9-phenyl-2,3,7-trihydroxy-6-fluorone (12 mg, 0.0379 mmol) in methanolic KOH of a bright magenta colour, was added. The solution was refluxed for 6 h and turned dark blue. After cooling to room temperature, the solvent was partly evaporated and the solution was chromatographed on LH 20. The electrodes were prepared according to a procedure published elsewhere[7]. Complex **2** was adsorbed in its anionic form from methanol. After having kept the electrode immersed in the warm solution (50 °C) for 24 h, it was rinsed quickly with methanol and dried in hot air.

RESULTS AND DISCUSSION

Complex 1

Electrochemistry

The electrochemical study of trinuclear complex **1** was complicated by its low solubility in polar organic solvents as well as by its chemical instability in coordinating solvents. The electrochemistry was investigated in water and in acetonitrile. In water, a two-electron anodic wave is observed (Fig. 1) and assigned to non-resolved one-electron oxidations of the two Ru-tetrammine units[3,4]. In acetonitrile, the reversible one-electron oxidation of the central [Ru(CN)$_2$(bpy)$_2$] unit is observed at $E_{1/2}$ = 1.25 V *vs* SCE. The complex is, however, unstable in this solvent, as shown by the appearance of a wave at 0.49 V *vs* SCE, attributed to the solvento complex [Ru(CH$_3$CN)-(NH$_3$)$_4$(py-COOH)]$^{2+}$. DPV measurements in water did not allow to resolve the Ru(II)/Ru(III) half wave potentials of the {Ru(NH$_3$)$_4$(py-COOH)} units, indicating a very low electronic coupling between the two metal moieties. From the DPV maximum an average $E_{1/2}$ value of 0.127 V was estimated.

Electronic Absorption Spectroscopy

As observed for the analogous species containing pyridine ligands at the Ru-ammine moieties[3,4], the visible absorption spectrum of trinuclear complex **1** in water is characterised by a MLCT band at 382 nm, and by an intense IT band at 743 nm involving the central {Ru^{II}(bpy)$_2$} and the two Ru^{III}-ammine units. Owing to the two-fold degenerate nature of this transition, its intensity is approximately twice that observed for the corresponding dinuclear species at 762 nm [7].

Electrochromic Behaviour

The electrochromic properties of complex **1** have been investigated both in aqueous solution and on $SnO_2(Sb)$ thin films supported on a conductive glass. The spectroelectrochemical measurements were performed in a three-electrode configuration (Pt counter-electrode and SCE reference electrode). On SnO_2 the complex displays a light blue-green colour and an absorption
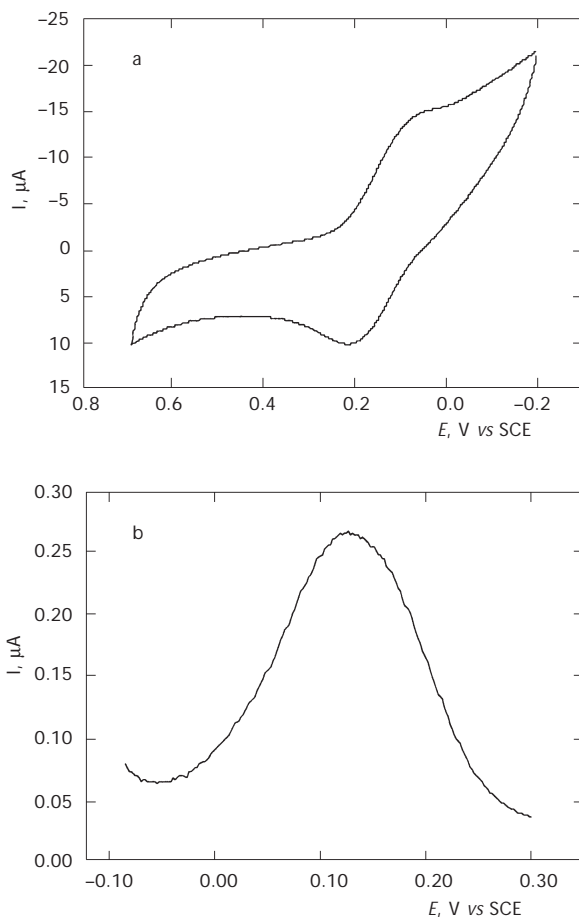

FIG. 1
a Cyclic voltammogram of complex **1**. Conditions: Pt working electrode, aqueous solution containing tetraethylammomium tetrafluoroborate, scan rate 0.1 V s^{-1}. b Differential pulse voltammogram of complex **1**. Conditions: Pt working electrode, aqueous solution containing tetraethylammomium tetrafluoroborate, scan rate 0.004 V s^{-1}, amplitude of 0.01 V

spectrum analogous to that observed in solution (Fig. 2). Application of a potential –0.5 V between the electrodes caused the white light transmittance of the device to decrease from 43 to 2%, with appearance of an intense red colour due to the bleaching of the IT band and a simultaneous intensity increase of a band at 512 nm. This band is assigned to Ru^{II}–py MLCT transitions localised on the $\{Ru(NH_3)_4(py\text{-}COOH)\}$ units, which overlap the MLCT transitions of the $Ru(bpy)_2^{2+}$ moiety. Distinct colour changes were observed in the potential range –0.5 to +1 V with switching times between the two limiting colours of the order of milliseconds. Stability tests in a sandwich-type electrochromic cell devices cycled between –0.5 and +1 V for 10 000 cycles indicate no appreciable changes of the transmittance in the visible region.

Complex *2*

Synthesis

The complex **2** was synthesised by treatment of $[Ru\{dcb(NBu_4)_2\}_2(MeOH)_2]$ with the protonated ligand (method *A*) or by treatment of $[RuCl_2(dcb_2)_2]$ with the deprotonated ligand (method *B*). Both methods yielded the same blue complex that was identified by MALDI-TOF mass spectrometry.
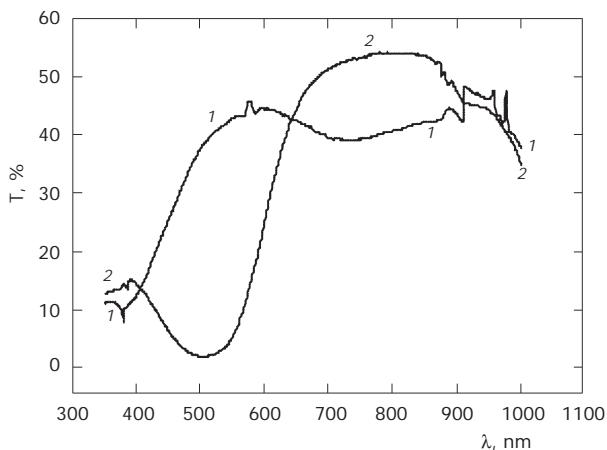
FIG. 2

Transmittance spectral changes in the visible-NIR region observed in an open three-electrode cell containing complex **1** adsorbed on an Sb-doped SnO_2 electrode, supported on FTO glass in CH_2Cl_2/0.1 M tetraethylammonium hexafluorophosphate: +1 V (*1*), –0.5 V (*2*)

Compared to the bpy analogue, the synthesis was complicated by the low solubility of the $[RuCl_2(dcbH_2)_2]$ starting material. The anionic form is significantly more soluble in methanol, but caution is necessary to add only four equivalents of the base because the complex is unstable under alkaline conditions. The product can be isolated by precipitation using HPF_6, but the fully protonated form exhibits a very low solubility in most common solvents. Therefore, it is preferable to transform the complex into the anionic form with Bu_4N^+ counterions, as accomplished by method *A*. In addition, it should be noted that the 9-phenyl-2,3,7-trihydroxy-6-fluorone shows poor solubility in most common solvents with the exception of DMF. After deprotonation, the ligand dissolves very well in methanol, but should be used immediately because it decomposes rather quickly under alkaline conditions.

Electrochemistry

Cyclic voltammetry of the protonated form of complex **2** in DMF shows two quasi-reversible, one-electron processes at $E_{1/2}$ = +0.04 and +0.38 V *vs* SCE. In addition, there are irreversible waves at potentials higher than 1 V *vs* SCE and more negative than –1.6 V *vs* SCE. This is in accordance with an earlier result for a related dinuclear Ni complex of 9-phenyl-2,3,7-trihydroxy-6-fluorone by Dei *et al.*[18] who reported two redox couples at –0.38 and +0.40 V *vs* Fc/Fc$^+$, with only the first wave fully reversible and assigned to a ligand-centred L^{3-}/L^{2-} couple. In contrast, Barthram and Ward[14] found three reversible waves in this region for the bpy analogue, two of which they attributed to processes centred on the bridging ligand. By further comparison, the other processes can be assigned as follows: (i) the irreversible waves at high negative potentials are due to reductions of the terminal dcb ligands and (ii) the irreversible wave at high positive potential is a metal-centred Ru(II)/Ru(III) process. In acetonitrile, deprotonated complex **2** reveals only one reversible wave at $E_{1/2}$ = –0.03 V *vs* SCE (Fig. 3). All other waves are irreversible with no return wave. This effect can be attributed to the adsorption of the complex on the electrodes, which is known to occur for carboxylate groups. However, since we are less concerned with the assignment of the various processes and more with the exploitation of the electrochromic potential, we have focussed on the reversible process around 0 V *vs* SCE and explored its spectroelectrochemical properties.

Spectroelectrochemistry

A spectroelectrochemical study of complex **2** in DMF was performed at room temperature, using an optically transparent thin-layer electrochemical (OTTLE) cell with a silver reference electrode, a Pt counter-electrode and a Pt working electrode. In the region between +0.25 and –0.15 V *vs* SCE, which spans the redox level of the L^{3-}/L^{2-} couple, complex **2** shows a strongly electrochromic behaviour with two main features: (i) a colour change in the visible region from blue (reduced state) to red (oxidised state) and (ii) the appearance of a new band in the NIR region upon oxidation (Fig. 4). This low-energy transition could tentatively be assigned to a Ru → semiquinone MLCT transition by comparison to the result reported by Barthram and Ward[14]. However, it should be again pointed out that a localised concept of the transitions in these "non-innocent" complexes is of limited validity. The L^{3-}/L^{2-} redox process is reversible, as indicated by the presence of several isosbestic points and the regeneration of the spectrum of the reduced compound at the end of the experiment.

Behaviour on ITO Glass

A 1.5 cm wide thin film of SnO_2/Sb was spread on an ITO glass as described elsewhere[7]. After drying, the glass was cut into stripes of 1 cm width. The glass was put into a cuvette filled with γ-butyrolactone and connected as
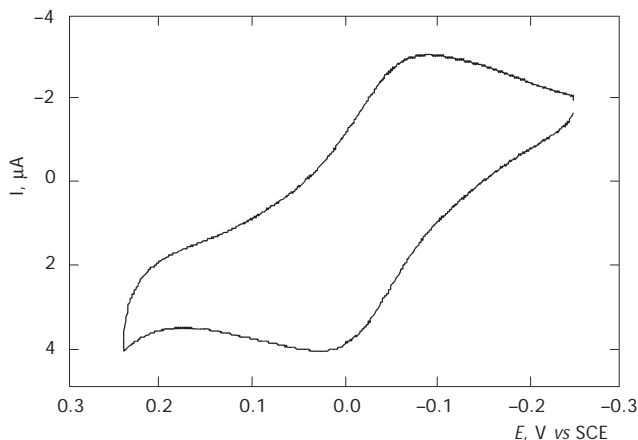

FIG. 3

Cyclic voltammogram of complex **2** in acetonitrile containing 0.1 M Bu_4NPF_6 as supporting electrolyte, using a glassy carbon working electrode, scan rate of 0.1 V s^{-1}

the working electrode of a standard three-electrode set-up with an Ag pseudoreference electrode and a Pt counter-electrode. The dye **2** adsorbed very well on a nanostructured thin layer of SnO_2/Sb due to the presence of the carboxylate groups that bind to the surface most likely through the ester groups. Using a standard three-electrode set-up with a silver wire as a pseu
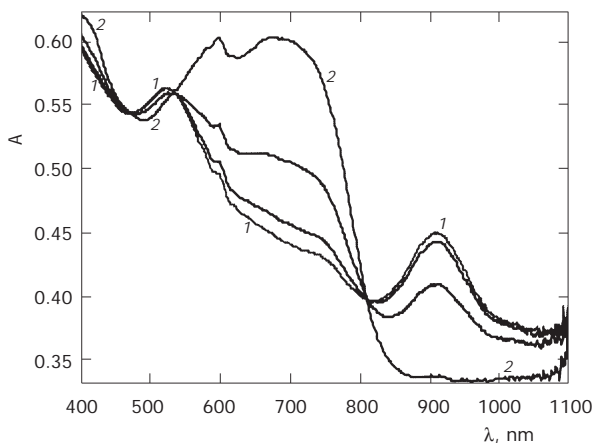

FIG. 4
Electronic spectra of complex **2** in DMF from a spectroelectrochemical study in an OTTLE cell with an Ag pseudoreference electrode, a Pt counter-electrode and a Pt working electrode. The line *1* shows the spectrum at +0.25 mV (L^{2-}), the line *2* the spectrum at –0.15 V (L^{3-})
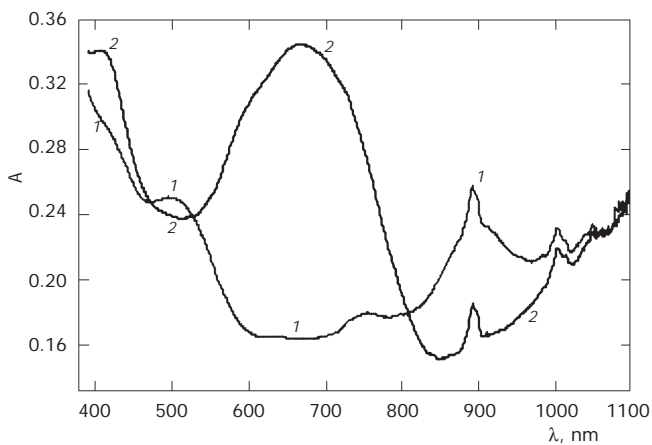

FIG. 5
Electronic spectra of complex **2** adsorbed on an Sb-doped SnO_2 electrode, supported on FTO glass in γ-butyrolactone and with $LiClO_4$ supporting electrolyte. The line *1* shows the spectrum at +0.2 mV (L^{2-}), the line *2* the spectrum at –0.2 V (L^{3-})

doreference electrode, a platinum wire as the counter-electrode and the ITO glass as the working electrode, we were able to induce very fast and sharp colour changes from blue (reduced) to red (oxidised) by switching the applied potential between +0.2 and –0.2 V (Fig. 5). However, while the contrast ratio, response time and colouration efficiency are promising, the colouration diminishes already after a few switching cycles. Since the redox process is shown to be reversible, it appears that the problem is mainly due to desorption of the complex. Our efforts now are therefore focussed on replacing the carboxylate groups with phosphonate or boronic ester groups that offer a stronger binding to the surface.

CONCLUSIONS

We have shown in this work that polynuclear metal complexes exhibiting an interesting electrochromic behaviour can be prepared and adsorbed on the surface of a nanocrystalline semiconductor. The spectroscopic properties of these molecular systems can be controlled and tuned by the synthetic design of coordinated and bridging ligands as well as of metal centres. The spectroelectrochemical behaviour of a novel dinuclear Ru complex containing the L^{3-} form of 9-phenyl-2,3,7-trihydroxy-6-fluorone (H_3L) as the bridging ligand, proves that this species can be reversibly oxidised in solution and the first oxidation (L^{3-}/L^{2-}) can be exploited on the surface of an SnO_2/Sb-covered ITO glass electrode. However, further work is needed in order to enhance its stability.

REFERENCES

1. Creutz C.: *Prog. Inorg. Chem.* **1983**, *30*, 1.
2. Hush N. S.: *Prog. Inorg. Chem.* **1967**, 8, 391.
3. Bignozzi C. A., Roffia S., Scandola F.: *J. Am. Chem. Soc*. **1985**, *107*, 1644.
4. Bignozzi C. A., Paradisi C., Roffia S., Scandola F.: *Inorg. Chem*. **1988**, *27*, 408.
5. Roffia S., Paradisi C., Bignozzi C. A.: *J. Electroanal. Chem. Interfacial Electrochem*. **1986**, *200*, 105.
6. Schonover J. R., Timpson C. J., Meyer T. J., Bignozzi C. A.: *Inorg. Chem*. **1992**, *31*, 3185.
7. Biancardo M., Schwab P. F. H., Argazzi R., Bignozzi C. A.: *Inorg. Chem*. **2003**, *42*, 3966.
8. Ward M. D., McCleverty J. A.: *J. Chem. Soc., Dalton Trans*. **2002**, 275.
9. Pierpont C. G.: *Coord. Chem. Rev*. **2001**, *216*, 99.

10. Lever A. B. P., Masui H., Metcalfe R. A., Stufkens D. J., Dodsworth E. S., Auburn P. R.: *Coord. Chem. Rev.* **1993**, *125*, 317.
11. Haga M., Dodsworth E. S., Lever A. B. P.: *Inorg. Chem.* **1986**, *25*, 447.
12. Joulié L. F., Schatz E., Ward M. D., Weber F., Yellowlees L. J.: *J. Chem. Soc., Dalton Trans.* **1994**, 799.
13. Barthram A. M., Cleary R. L., Kowallick R., Ward M. D.: *Chem. Commun.* **1998**, 2695.
14. Barthram A. M., Ward M. D.: *New J. Chem.* **2000**, *24*, 501.
15. Bignozzi C. A., Biancardo M., Schwab P. F. H. in: *Molecular and Supramolecular Photochemistry* (V. Ramamurthy and K. S. Schanze, Eds), Vol. 10. Marcel Dekker, New York 2003.
16. Demas J. N., Turner T. F., Crosby G. A.: *Inorg. Chem.* **1969**, *8*, 674.
17. Liska P., Vlachopoulos N., Nazeeruddin K. M., Comte P., Graetzel M.: *J. Am. Chem. Soc.* **1988**, *110*, 3686.
18. Dei A., Gatteschi D., Pardi L.: *Inorg. Chim. Acta* **1991**, *189*, 125.