Inorg. Chem. **2003**, *42*, 3966–3968

Inorganic Chemistry
Communication

Electrochromic Devices Based on Binuclear Mixed Valence Compounds Adsorbed on Nanocrystalline Semiconductors

Matteo Biancardo,[†] Peter F. H. Schwab,[†] Roberto Argazzi,[‡] and Carlo Alberto Bignozzi*,[†]

Dipartimento di Chimica and I.S.O.F., Università di Ferrara, Via L. Borsari, 46, Ferrara, Italy

Received February 11, 2003

A series of cyano-bridged binuclear mixed valence complexes of the general formula M–$Ru^{III}(NH_3)_4$pyCOOH [pyCOOH = isonicotinic acid; M = *cis*-$Ru(bpy)_2(CN)_2$, **1** (bpy = 2,2′ bipyridine); *trans*-$Ru(py)_4(CN)_2$, **2** (py = pyridine); $[Ru(CN)_6]^{4-}$, **3**; $[Fe(CN)_6]^{4-}$, **4**] have been prepared and anchored through the carboxylic function to nanocrystalline TiO_2 or SnO_2 electrodes. The complexes display a reversible electrochromic behavior in the range of applied potential from –0.5 to +0.5 V, versus SCE. Tuning of the electronic transitions in the visible and near-infrared spectral regions is achieved through changes of the solvent and of the cyano-bridged metal moiety M.

The research field of electrochromic compounds is very broad and includes inorganic, organic, and polymeric materials as well as several hybrid materials.[1] From an applicative standpoint, electrochromic devices hold much promise, and several areas of interest have been proposed and are currently under investigation and development.[2]

Recently, substituted viologens containing PO_3H_2 or COOH functions have been used in electrochromic devices that try to combine the advantages of nanocrystalline metal oxide films with those of redox chromophores.[3−6] A monolayer of diphosphonoethyl substituted viologen is hereby chemisorbed onto a nanostructured TiO_2 film on an indium tin oxide (ITO) electrode. Since the redox potential of the viologen lies above the conduction band edge of TiO_2 at the liquid−solid interface, electrons can be transferred reversibly from the conduction band to the molecule, and the semiconductor becomes conducting for the adsorbed species.

Optical electron-transfer transitions in multinuclear metal complexes have been studied very broadly and thoroughly.[7−11] Numerous binuclear, and more generally, polynuclear mixed valence compounds based on transition metal ions have been reported since the synthesis of the Creutz ion, $[Ru^{II}(NH_3)_5\text{-}pzRu^{III}(NH_3)_5]^{5+}$.[11] In weakly coupled unsymmetrical mixed valence complexes,[12] the optical band energy (E_{op}) at λ_{max} of the metal-to-metal charge-transfer bands (MMCTs), also known as intervalence transfer bands (ITs), is given by $E_{op} = \chi_i + \chi_o + \Delta E$, where χ_i and χ_o are the classical inner-sphere and outer-sphere vibrational reorganization and ΔE is the internal energy difference between the two oxidation state isomers. As a consequence, modulation of the transmitted light over the whole visible and NIR spectral regions can be obtained by changes of the solvent (χ_o) or of the metal complex or modifications of the coordination sphere, which will mainly affect the magnitude of χ_i and ΔE.

In the present communication, we would like to present the synthesis and the spectroscopic properties of binuclear cyano-bridged mixed valence compounds which display electrochromic behavior when chemisorbed onto transparent nanocrystalline SnO_2 or TiO_2 films on conductive glass. The complexes show a series of absorption bands, due to electronic transitions localized on the metal subunits and to electronic transitions between the metal centers, whose intensity can be modulated by the applied potential. The phenomenon can be applied to control color changes in the whole visible and near-infrared regions.

The general principle that we have followed in the molecular design of the polynuclear species is based on the introduction of a metal containing moiety which can be directly bound to the surface of the semiconductor and can

---

* Address correspondence to this author. E-mail: g4s@unife.it.

[†] Dipartimento di Chimica.

[‡] I.S.O.F.

(1) Bignozzi, C. A.; Biancardo, M.; Schwab, P. F. H. In *Semiconductor Photochemistry and Photophysics. Vol. 10 of Series: Molecular and Supramolecular Photochemistry*; Ramamurthy, V., Schanze, K. S., Eds.; Marcel-Dekker: New York, 2003.

(2) (a) Green, M. *Chem. Ind.* **1996**, *17*, 641. (b) Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. In *Electrochromism: Fundamentals and Applications*; VCH: Weinheim, 1995. (c) Mortimer, R. J. *Chem. Soc. Rev.* **1997**, *26*, 147.

(3) Marguerettaz, X.; O'Neill, R.; Fitzmaurice, D. *J. Am. Chem. Soc.* **1994**, *116*, 2629.

(4) Cinnsealach, R.; Boschloo, G.; Rao, S. N.; Fitzmaurice, D. *Sol. Energy Mater. Sol. Cells* **1998**, *55*, 215.

(5) Cinnsealach, R.; Boschloo, G.; Rao, S. N.; Fitzmaurice, D. *Sol. Energy Mater. Sol. Cells* **1999**, *57*, 107.

(6) Grätzel, M. *Nature* **2001**, *409*, 575.

(7) Taube, H. *Ann. N.Y. Acad. Sci.* **1978**, *313*, 418.

(8) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94.

(9) Bignozzi, C. A.; Roffia, S.; Scandola, F. *J. Am. Chem. Soc.* **1985**, *107*, 1644.

(10) Bignozzi, C. A.; Paradisi, C.; Roffia, S.; Scandola, F. *Inorg. Chem.* **1988**, *27*, 408.

(11) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1

(12) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

10.1021/ic034145t CCC: $25.00

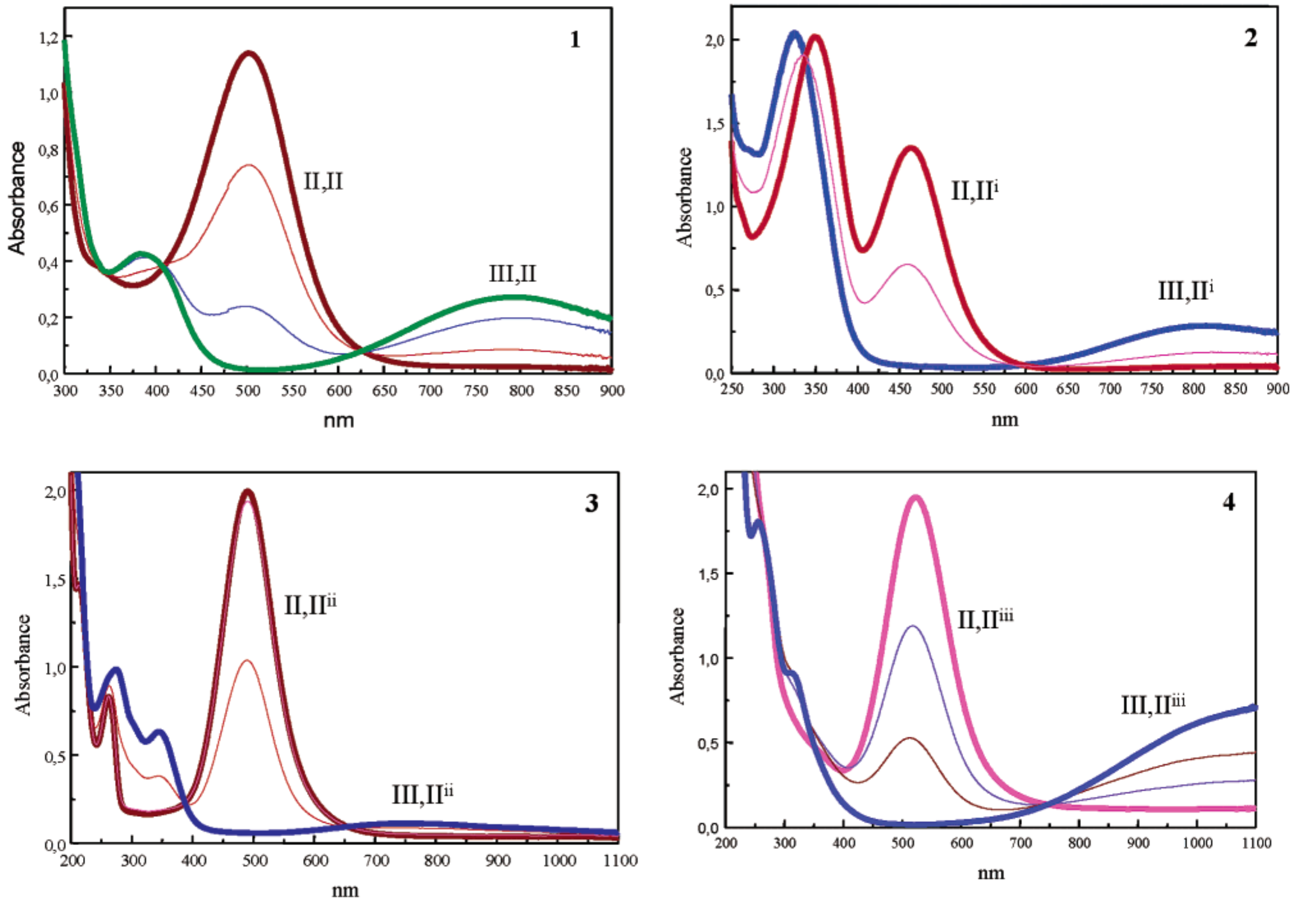
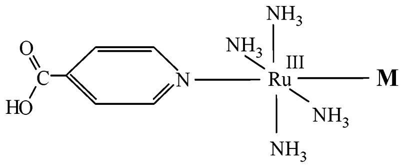


Figure 1. Absorption spectral changes of the binuclear mixed valence ruthenium complexes **1**−**4** in aqueous solution. The reduced [(II,II), (II,II^{i}), (II,II^{ii}), (II,II^{iii})] species were produced in the presence of Zn amalgam. Reoxidation of the binuclear species was performed by using H_2O_2.

be interconverted between two oxidation states at a potential close to 0 V versus SCE. This arrangement maximizes the electronic coupling between the molecular system and the semiconductor and promotes color changes by applying only a small potential difference between the electrodes, a feature considered relevant in regard to low power consumption. On the basis of this idea, the cyano-bridged complexes of the following general formula have been prepared and tested:



Here, M = *cis*-Ru(bpy)$_2$(CN)$_2$, **1** (bpy = 2,2′ bipyridine); *trans*-Ru(py)$_4$(CN)$_2$, **2** (py = pyridine); [Ru(CN)$_6$]$^{4-}$, **3**; [Fe(CN)$_6$]$^{4-}$, **4**.

The syntheses (see Supporting Information, S1) have been carried out under mild conditions, by treating [*trans*-Ru(NH$_3$)$_4$(isn)(SO$_4$)]Cl (isn = isonicotinic acid)[13] with cyanide containing complexes in the presence of zinc amalgam under argon atmosphere. The cyclic voltammograms of all species in water solution show a reversible electrochemical behavior, with the first wave in the potential range 0−200 mV versus SCE assigned to the Ru(II)/(III) couple of the Ru(NH$_3$)$_4$ moiety (Table 1).

Table 1. Redox and Spectroscopic Properties in H_2O of Ru Mixed Valence Binuclear Complexes of the Type M−Ru^{III}(NH$_3$)$_4$pyCOOH

M	$E_{1/2}{}^{a}$ Ru(NH$_3$)$_4{}^{II/III}$	E_{op} (cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})
Ru^{II}(py)$_4$CN$_2$	0.18	13160	4980
Ru^{II}(bpy)$_2$CN$_2$	0.11	12500	4500
Ru^{II}(CN)$_6$	0.10	12350	5600
Fe^{II}(CN)$_6$	0.06	8700	6000

[a] Redox potential vs SCE determined in a conventional three electrode cell by using 0.1 M tetraethylammonium tetrafluoroborate as supporting electrolyte, glassy carbon as working electrode, and platinum as counter electrode.

The spectroscopic properties have been characterized both in aqueous solution and on TiO_2 or SnO_2 thin films supported on conductive glass (see Supporting Information, S2). All species display a broad IT band, typical of class II mixed valence complexes with half widths ($\Delta\nu_{1/2}$) of the order of 4500−6000 cm^{-1} (Table 1). The binuclear species display a metal-to-metal Ru^{II} → Ru^{III} charge-transfer band in the one electron oxidized form, rendering them green (**1**) or blue (**2**, **3**, **4**) in color. Upon going from the oxidized to the reduced species, the Ru(II) → Ru(III) IT bands are quenched, and the colors of the complexes are determined by the presence of $d\pi-\pi^*$ (Ru → py) MLCT bands, resulting in color changes to red for **1** and **4**, or red-violet for **2** and **3**. The spectral changes observed for the four binuclear complexes

---

(13) Vogt L. H.; Katz, J. L.; Wiberley, S. E. *Inorg. Chem.* **1965**, *4*, 1157.

in water solution (Figure 1) occur in all cases with isosbestic points, indicating interconversion in a single step without intermediates. Analogous spectral changes were observed with the species adsorbed on transparent TiO_2 or SnO_2 thin film electrodes, although of lower quality due to the light scattering of the nanocrystalline substrate. These spectroelectrochemical measurements[14] revealed distinct color changes in a narrow potential range (−0.5 to +0.5 V vs SCE), with switching times between the two limiting colors on the order of milliseconds. Stability tests performed in sandwich type cells containing the dyes adsorbed on SnO_2/Sb electrodes demonstrated a high stability, with optical density changes lower than 2% after cycling the electrochromic device 12000 times between 0 and −1 V.

Owing to the presence of the amine and cyanide ligands, known to give rise to specific donor−acceptor interactions with solvents,[15−19] an interesting solvatochromic behavior was observed for these species. For complex **1**, the spectral changes are dominated by amine interactions with the solvents as shown by the linear correlation of the solvent donor number[20,21] with the IT band maxima and with the half-wave potential of the ruthenium amine moiety (Table 2).

Table 2. Solvatochromic Effect on the Spectroscopic Properties of the Binuclear Complex *cis*-$Ru(bpy)_2(CN)_2Ru^{III}(NH_3)_4pyCOOH$ (**1**)

solvent	DN	MLCT λ_{max} (nm)	MMCT λ_{max} (nm)	$E_{1/2}$ (mV) (vs SCE)
CH_2Cl_2	0	399	900	360
CH_3CN	14.1	428	844	340
$(CH_3)_2CO$	17	404	817	285
DMF	26.6	497	699	127.5
H_2O	33	389	762	110

It can be concluded that this type of polynuclear species in general possesses a high degree of flexibility thanks to the possibility of tuning its spectroscopic properties through changes of metal centers, of coordinated or bridging ligands, and of solvents. The availability of a fast screening protocol to test suitable ligand/metal combinations for tuning their properties should be of considerable utility. We are currently investigating a series of binuclear and trinuclear complexes containing a combination of metal centers and of coordinated ligands and developing additional synthetic routes for anchoring the polynuclear species through phosphonic and boronic acid units.

Acknowledgment. We thank Prof. D. Fitzmaurice (UCD Ireland) and Dr. D. Corr for help and guidance in the stability tests. We acknowledge financial support from Nanomat (now NTera L.t.d.) and from E.U. Micro−Nano Project HPRN-CT-2000-00028.

Supporting Information Available: Listings of preparations of compounds, preparations of nanoparticles, preparation of electrodes, assembly of devices, and stability test of devices. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034145T

---

(14) The spectroelectrochemical measurements were either performed in a three electrode configuration (with a Pt counter and SCE reference electrode) or in sandwich type cells formed by two sheets of FTO glass 5 × 5 cm^2 and separated by a 200 μm thick polymer seal made of Surlyn. In both cases, the working electrodes with the adsorbed electrochromic compounds were prepared by depositing a 6 μm thick nanoporous film of TiO_2 or of Sb-doped SnO_2 colloid that was heated at 450 °C for 30 min in the presence of air on FTO. The electrode was then cooled at room temperature and immersed overnight in a methanol solution containing the binuclear dye. Dye adsorption was enhanced by heating the solution for 3 h. After the sandwich cell was assembled, the space between the electrodes was filled with a γ-butyrolactone solution containing 0.05 M lithium perchlorate, and 0.02−0.05 M ferrocene.

(15) Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 224.

(16) Bignozzi, C. A.; Chiorboli, C.; Indelli, M. T.; Rampi Scandola, M. A.; Varani, G.; Scandola, F. *J. Am. Chem. Soc.* **1986**, *108*, 7872.

(17) Indelli, M. T.; Bignozzi, C. A.; Marconi, A.; Scandola, F. *J. Am. Chem. Soc.* **1988**, *110*, 7381.

(18) Davila, J.; Bignozzi, C. A.; Scandola, F. *J. Phys. Chem.* **1989**, *93*, 1373.

(19) Timpson, C. J.; Bignozzi, C. A.; Sullivan, B. P.; Kober, E. M.; Meyer, T. J. *J. Phys. Chem.* **1996**, *100*, 2915.

(20) Gutmann, V.; Resch, G.; Linert, W. *Coord. Chem. Rev.* **1982**, *43*, 133.

(21) The donor number (DN) of a solvent is defined as the enthalpic change at 25 °C for formation of the adduct between $SbCl_5$ and the solvent in 1,2-dichloroethane.