

Novel Ru-Dioxolene Complexes as Potential Electrochromic Materials and NIR Dyes

Peter F. H. Schwab,* Sara Diegoli, Matteo Biancardo, and Carlo Alberto Bignozzi

Dipartimento di Chimica, Università di Ferrara, Via L. Borsari, 46, Ferrara, Italy

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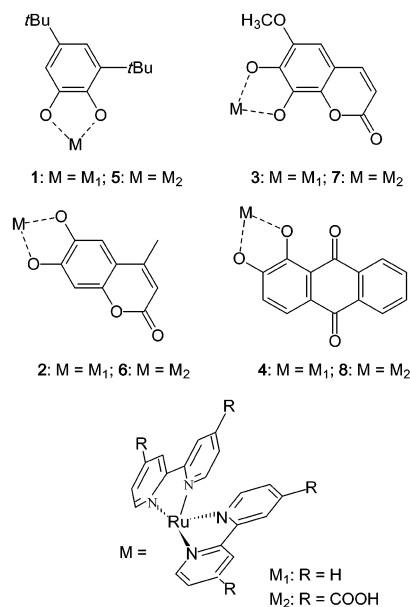
A series of Ru(bpy)₂-dioxolene complexes **1–4** (bpy = 2,2'-bipyridine) and corresponding Ru(dcb)₂-dioxolene complexes **5–8** (dcbH₂ = 2,2'-bipyridine-4,4'-dicarboxylic acid) have been prepared, and their spectroelectrochemical behavior in solution has been investigated. The complexes show reversible electrochemical behavior accompanied by a strong NIR absorption in their semiquinone forms due to a Ru(dπ) → sq(π*) MLCT band. Complete quenching of the NIR absorption occurs both upon oxidation (to the quinone form) and upon reduction (to the catechol form) very close to 0 V. The color of the systems can be tuned by using a wide range of ligands. The complexes **5–8** can be anchored onto nanocrystalline inorganic semiconductors allowing incorporation into potential electrochromic devices. As a proof of principle, compound **8** has been adsorbed on nanocrystalline Sb-doped SnO₂ supported on FTO glass, and it displays reversibly switchable electrochromic behavior in the NIR.

Redox-switchable molecular systems that display distinct changes in their absorption spectra as a function of the oxidation state are of considerable interest to chemists and material scientists.¹ Depending on the region of the absorption spectra that can be manipulated, such electrochromic compounds could be utilized, for example, in displays if they cover the UV–vis region or in optoelectronics if the switchable bands lie in the NIR region. Few examples of electrochromic materials in the NIR are known,² among them some conducting polymers.³ Due to their very interesting spectroelectrochemical behavior, 1,2-dioxolene-containing Ru complexes have been intensely investigated in this context.^{4–6} Lever's work has demonstrated that ligand-based redox processes between the catecholate (cat), semiquinonate (sq), and quinone (q)

forms are responsible for the different oxidation states while the metal center remains in the +2 oxidation state throughout.⁷ The complexes display a strong NIR absorption in their semiquinone forms due to a Ru(dπ) → sq(π*) MLCT band which is quenched both upon oxidation (to the quinone form) and upon reduction (to the catechol form).^{8–10}

In our ongoing effort¹¹ to develop electrochromic devices,^{3,12} we have synthesized a series of Ru(bpy)₂-dioxolene complexes, **1–4**, and investigated their spectroelectrochemical behavior in solution. In addition, we have prepared the analogous compounds **5–8** where 2,2'-bipyridine-4,4'-dicarboxylic acid ligands have replaced the bpy ligands, functioning as anchors to a nanocrystalline inorganic semiconductor surface, such as Sb-doped SnO₂. We have selected dioxolene ligands that represent large classes of dyes in order to have access to a pool of similar compounds allowing us to fine-tune the properties of the complexes by simple replacement of the ligand.

As reference point, [Ru(bpy)₂(di-*tert*-butyl-cat)] (**1**) was chosen since its electrochromic behavior in the NIR has been documented.⁷ The other ligands used in this study are alizarin, 7,8-dihydroxy-6-methoxy-coumarin, and 6,7-dihydroxy-4-methyl-coumarin.



* To whom correspondence should be addressed. E-mail: swp@dns.unife.it.

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Table 1. Redox and Spectroscopic Properties in Acetonitrile of Ru(bpy)₂-dioxolene Complexes

	$E_{1/2}^a$ cat/sq	$E_{1/2}^a$ sq/q	MLCT Ru → sq λ_{\max} (nm)
1	-0.63	+0.11	876
2	-0.06	+0.76	974
3	-0.02	+0.73	948
4	+0.12	+0.92	942

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

The syntheses (S1 in the Supporting Information) of the bpy-containing species have been carried out under mild conditions, starting from Ru(bpy)₂Cl₂ which was treated with the respective ligand in methanolic solution after the chlorides had been precipitated with Tl(OAc). The complexes were purified by precipitation as their PF₆ salts and characterized by IR, MS, and cyclic voltammetry. The cyclic voltammograms of all species in acetonitrile solution show reversible electrochemical behavior, with one wave in the potential range between 700 and 1000 mV versus SCE, and a second wave in the potential range around 0 V versus SCE (Table 1), with the exception of **1**, where the potentials are shifted by about -0.5 V.

The first redox couple can be assigned to the transforma-

tion between the semiquinone and quinone form of the ligand, the second redox couple to the semiquinone/catechol transition.

The spectroelectrochemical properties have been characterized in an OTTLE cell using acetonitrile as the solvent and Bu₄NPF₆ as the base electrolyte (Figure 1). All species display the expected Ru(dπ) → sq(π*) MLCT band that can be activated and deactivated reversibly by simply switching between a positive and negative bias very close to 0 V versus SCE. The spectroelectrochemical measurements show several isosbestic points in all cases, demonstrating that the processes occur in one step and are completely reversible. It is worth noting that the maximum of the NIR band is a function of the dioxolene ligand and ranges from 880 to about 974, showing appreciable variation both between ligand families and among them as demonstrated by the coumarin dyes. We therefore expect to be able to fine-tune the absorption peak over a wide range in the NIR region. In addition to the distinct activation and deactivation of the band in the NIR, there are noticeable changes in the visible region of the spectrum, as well. Especially, the alizarin complex shows a sharp color change from blue to yellow upon oxidation. In principle, color changes should be adjustable through changes of the substituents on the core dioxolene ligand.

The synthesis of the dcb analogues is complicated by the

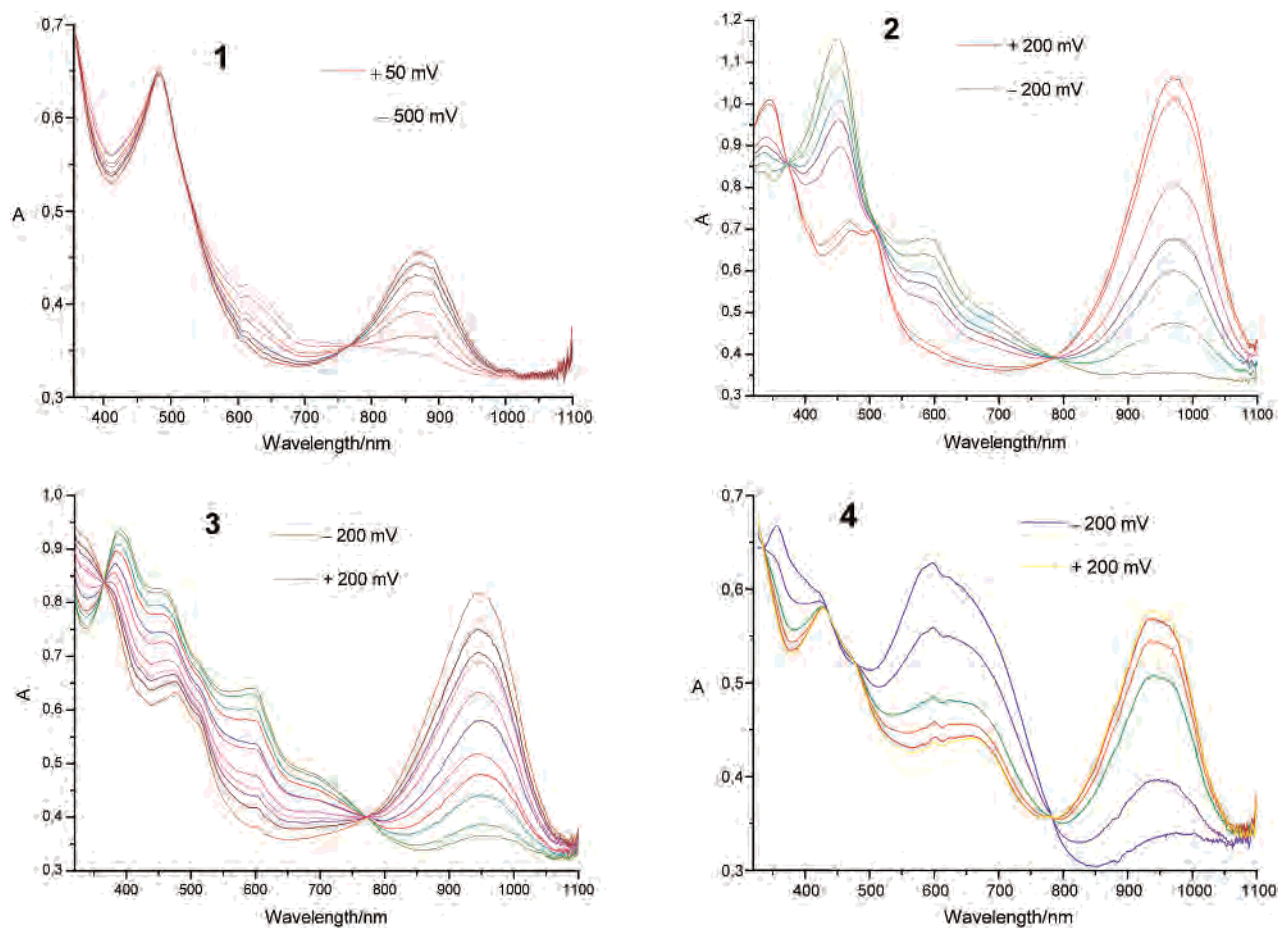


Figure 1. Absorption spectral changes of the Ru(bpy)₂ dioxolene complexes **1–4** in acetonitrile solution. The spectroelectrochemical measurements were performed at room temperature using an OTTLE cell with Ag reference, Pt counter, and Pt working electrodes. The solution was degassed by bubbling argon through the cell for 30 min.

Table 2. Redox and Spectroscopic Properties in Acetonitrile of Ru(dcb)₂–Dioxolene Complexes

	MLCT Ru → sq λ _{max} (nm)	E _{1/2} (mV) (vs SCE)
5	892	− 0.49
6	978	− 0.11
7	953	− 0.19
8	945	+ 0.01

low solubility of the [Ru(dcbH₂)₂Cl₂]¹³ starting material. Since the anionic form is significantly more soluble in polar organic solvents, the conversion to the NBu₄ salt by treatment with NBu₄OH in methanol is advantageous. Excess base, however, should be avoided due to the instability of the dioxolene ligands prior to binding. For characterization, the complexes can be precipitated by addition of HPF₆. The electrochemical measurements are more intricate because the anionic form tends to adsorb on the working electrode, especially at higher potentials. The waves of the sq/cat couples close to 0 V, however, were shown to be reversible in all cases (Table 2), allowing their spectroelectrochemical characterization. Compared to the bpy species, analogous spectral changes in the NIR were observed with the dcb complexes, while the absorption maximum of the NIR band was consistently red-shifted by less than 10 nm. Again, the

reversibility of the processes was verified by the presence of several isosbestic points and the exact regeneration of the spectrum upon reversal of the bias (Figure S1). The complexes can be anchored to the surface of a nanocrystalline inorganic semiconductor, such as Sb-doped SnO₂.¹⁴ For example, compound **8** adsorbs well onto the surface from an acetonitrile solution, and the MLCT band in the NIR (λ_{max} = 956 nm) can be reversibly switched by applying a potential between +500 and −50 mV (Figure S2). We are currently optimizing the conditions of the films in order to employ the species in electrochromic devices.

In summary, our work presents novel Ru–dioxolene complexes that show interesting reversible electrochromic behavior in the visible and especially in the NIR region with a switching potential of the sq/cat couple very close to 0 V. We have furthermore shown a way to immobilize these species on the surface of a nanocrystalline inorganic semiconductor by incorporation of carboxylate groups into the structures. In general, the systems possess a high degree of variability since the ligands employed represent large classes of organic dye molecules which should allow the fine-tuning of desired spectroelectrochemical properties. We are currently investigating these correlations in more detail and optimizing conditions for the electrochromic devices. In this context, the polyelectrochromic behavior, especially of the alizarin derivatives, will be investigated. In addition, we are exploring the emissive behavior of the coumarin species as a function of the oxidation state. The described properties should make these species interesting candidates for use in redox-switchable dyes and sensors for optoelectronic devices.

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Supporting Information Available: Listings of preparations of compounds, cyclic voltammograms, and spectroelectrochemical measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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