

Novel Self-Assembled Monolayers of Dipolar Ruthenium(III/II) Pentaammine(4,4'-bipyridinium) Complexes on Ultrathin Platinum Films as Redox Molecular Switches

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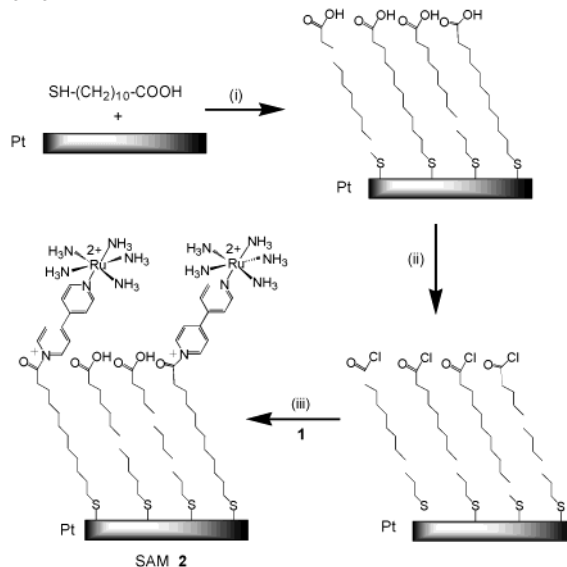
The synthesis of nanocomposite functional materials¹ is attracting growing interest in the emerging field of molecular electronics.² In this context, the concept of switching of a molecular property, “molecular switch”, is of relevance for the design and development of new optoelectronic nanodevices.³ Various examples of molecular switches have been reported in the literature. Most of them are based on either photoinduced or electroinduced processes often associated with changes of the molecular structure, for example, isomerization, proton transfer, or redox reactions.⁴ However, the majority of these studies are related to investigations in solution or in liquid crystals, with the exception of various examples of nanocomposite systems immobilized on metal electrodes.^{4b}

Metal complexes are suitable to molecular switches⁵ by virtue of electronic properties associated with the metal center.⁶ For instance, it has recently been demonstrated that dipolar ruthenium(II) amine complexes, *trans*-Ru^{II}(NH₃)₄L (L = axial ligand), of 4,4'-bipyridinium ligands can be reversibly and readily oxidized to their electron-deficient Ru^{III} analogues, either chemically or electrochemically.⁷ This is accompanied by a dramatic change of their optical properties. Indeed, while Ru^{II} complexes possess distinct linear (absorption maxima in the 580–640 nm region) and nonlinear optical features associated with their intense, low energy metal-to-ligand charge-transfer (MLCT) electronic transitions, Ru^{III} analogues are transparent in the whole visible region and possess negligible second-order optical nonlinearity.⁷ Therefore, these metal complexes are very intriguing candidates for designing nanocomposite molecular switches.

Here we report on novel self-assembled monolayers (SAMs) of redox-switch dipolar ruthenium(III/II) pentaammine(4,4'-bipyridinium) complexes on ultrathin, optically transparent platinum films. To the best of our knowledge, this represents the first example of a reversible molecular switch self-assembled on an optically transparent metal electrode, whose change in molecular properties can be simply detected with a conventional spectrophotometer.

Ultrathin platinum films (10 nm nominal thicknesses) on transparent glass slides were obtained by cool argon sputtering and used as substrates for monolayer self-assembly. These Pt substrates are particularly appropriate for an easy monolayer characterization by transmission UV/vis spectroscopy. In fact, they display an optical transparency (transmittance of ca. 0.70) in the visible spectral region and, different from gold ultrathin films, have the advantage of being only slightly affected by the metal surface plasmon absorption in such a region.⁸ Atomic force microscopy (AFM) measurements indicate that these ultrathin films have a continuous distribution of polycrystalline platinum (see Supporting Information) with a root-mean-square roughness of ca. 3.5 nm.⁹

Scheme 1^a



^a Conditions: (i) CH₂Cl₂, 25 °C, 20 h; (ii) SOCl₂, 40 °C, 5 h; (iii) DMF, 45 °C, 20 h.

The three-step synthetic approach to the synthesis of ruthenium pentaammine 4,4'-bipyridinium SAMs is reported in Scheme 1. It involves (i) chemisorption of 11-mercapto undecanoic acid, coupling layer, on the Pt substrate, (ii) appropriate derivatization of the acid to the corresponding acyl chloride by reaction with SOCl₂, and (iii) reaction with [Ru^{II}(NH₃)₅-4,4'-bipyridine](PF₆)₂ (**1**),¹⁰ to effect quaternization.

Aqueous contact angle (θ_a) measurements after step i reveal that θ_a changes from 75° for the Pt substrate to less than 10° for the thiol functionalized surface. This finding is consistent with the presence of carboxylic headgroups, in accordance with analogous results obtained for alkanethiol SAMs on bulk Au and Pt substrates.¹¹ X-ray photoelectron spectroscopy (XPS) measurements after step ii show that the chlorine(2p):sulfur(2p) ratio is ca. 1:1, indicating a quantitative acylation.

The appearance of a distinct absorption band at 588 nm after step iii (Figure 1) is diagnostic of the quaternization of **1** with formation of the Ru^{II}(NH₃)₅-4,4'-bipyridinium monolayer (SAM **2**). Actually, the comparison of optical absorption spectra in aqueous solution of **1** and those of the related [Ru^{II}(NH₃)₅-*N*-methyl-4,4'-bipyridinium](PF₆)₃ (**3**) indicates a remarkable red shift of 97 nm of the lowest MLCT absorption maximum upon quaternization (Figure 2). Therefore, the comparison of absorption spectra of **3** and SAM **2** (Figures 1, 2) provides unambiguous evidence that quaternization occurred. Moreover, the lack of any evident shoulder in the absorption spectrum of SAM **2** indicates the absence of

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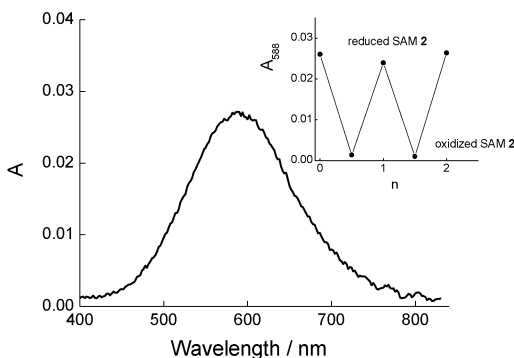


Figure 1. Absorption spectrum of SAM 2 recorded using as a reference sample the same ultrathin Pt substrate before step i. The inset shows the redox-switching of the absorbance maximum response with chemical oxidation by Ce^{IV} and reduction by N_2H_4 . n = number of redox cycles.

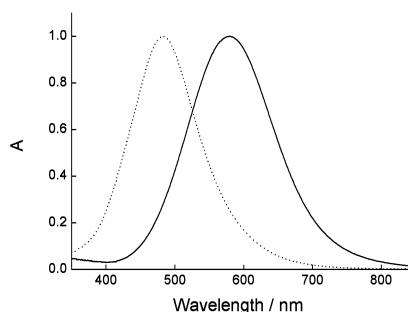
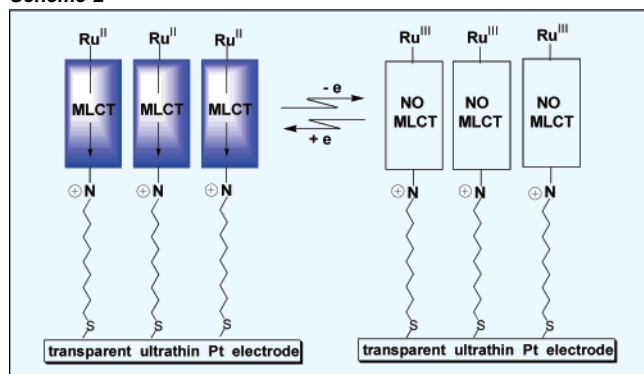


Figure 2. Normalized absorption spectra of $[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{-4,4'-bipyridine}](\text{PF}_6)_2$, **1** (dashed line), and the related quaternized compound $[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{-N-methyl-4,4'-bipyridinium}](\text{PF}_6)_3$, **3** (solid line), in aqueous solution.

Scheme 2



unreacted complex **1** adsorbed on the film surface. In addition, reaction of **1** with the Pt substrate without the coupling layer, under experimental conditions identical to those of step iii, does not give rise to any detectable absorption bands in the visible region, thus ruling out a chemical absorption of **1** on the platinum surface.

XPS measurements on SAM 2 were used to check the degree of quaternization after step iii. On the basis of the ruthenium(3d): sulfur(2p) ratio, the degree of quaternization of **1** is ca. 20% with respect to the thiol functionalized surface.

The suitability of SAM 2 as reversible molecular switches was tested by consecutive $\text{Ru}^{\text{II/III}}$ redox reactions. This was achieved

by using the appropriate oxidizing or reducing agents. Specifically, aqueous solutions of cerium(IV) sulfate and hydrazine were used as oxidizing and reducing agents, respectively.¹² Alternate oxidation/reduction cycles, obtained upon immersion of SAM 2 in the above redox solutions, result in the almost complete disappearance/restoration of the MLCT optical absorption band (see inset Figure 1).¹³ As pictorially depicted in Scheme 2, these findings provide clear and direct evidence that a reversible redox-switching, accompanied by significant changes of the optical properties, of the Pt-modified monolayer occurs upon chemical redox treatment.

In summary, in this paper we have shown the first example of a reversible molecular switch self-assembled on an optically transparent metal electrode, whose change in molecular properties can be simply detected by transmission spectroscopy with a conventional spectrophotometer. This represents an appealing model system in the perspective of integrated molecular switch nanodevices.

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Supporting Information Available: Details of experimental procedures and AFM analysis (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) We emphasize that the present work focuses on the reversible molecular switching of a self-assembled monolayer on an optically transparent metal electrode. Therefore, the effects of the morphological features of the Pt substrate on the overall optical properties of the SAM would be out of the aim of the present study. Such effects will be the object of a forthcoming investigation.
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- (12) Different from the study of Coe and co-workers⁷ carried out in solution on complex **3**, we used a Ce^{IV} solution as an oxidizing agent ($E^\circ(\text{Ce}^{\text{IV/III}}) = 1.76$ V) instead of H_2O_2 . In fact, we experienced that treatment of SAM 2 with H_2O_2 provoked significant irreversible damaging of the film.
- (13) An analogous behavior was observed for aqueous solutions of **3** after alternate oxidation/reduction cycles performed by using the above chosen redox agents.

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