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Chemical Communication between Metal-Complex-Based Monolayers**

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Communication involves highly complex processes that allow living systems and various devices to transfer information. Stimuli-responsive organic materials, in which changes in the molecular units are additive and generate a coherent response to an external stimulus (e.g., light, heat, metal ions, pH value, electric field) may serve as excellent systems to develop new artificial communication systems between two or more interfaces.[1,2] During the last three decades, much research has focused on chemically modifying various substrate surfaces with organic monolayers to control the substrate surface properties.[3,4] This approach has led to hybrid organic–inorganic materials with unique electronic/optical and structural properties[5–15] and even to biological model systems.[16–19] Intermolecular communication within thin films has been explored.[20] To date, little attention has been devoted to the transfer of information between self-assembled organic or polymeric surfaces.[21–25] A rare example is the three-phase test for reaction intermediates designed by Rebek and co-workers, in which an intermediate is generated from a polymer-bound precursor and detected by trapping on another solid phase.[23–25] Herein, we demonstrate long-range electron transfer between two redox-active monolayer-based interfaces using a metal ion as an electron carrier and an optical readout to determine the oxidation state and the active surface area of the system. More specifically, the system consists of two analogous osmium (**1**, **2**) and ruthenium (**3**, **4**) polypyridyl complexes covalently immobilized on two glass substrates.

The siloxane-based monolayers **1**–**4** (Figure 1) were formed by previously reported procedures[26] and were characterized by a series of surface analysis methods, including atomic force microscopy (AFM), ellipsometry, and UV/Vis spectroscopy.[26–29] We have demonstrated that the osmium centers of monolayer **1** can be oxidized within minutes from Os^{2+} to Os^{3+} by trace amounts of $FeCl_3$ in organic solvents such as acetonitrile to generate Fe^{2+} and system **2** with concurrent bleaching of the metal-to-ligand charge-transfer (MLCT) bands.[28] The highly robust monolayer can be reset (**2**→**1**) by washing with water for less than one minute. Interestingly, the new ruthenium-based monolayers (**3**) are highly sensitive to reduction from Ru^{3+} to Ru^{2+} (**3**→**4**) by parts per million (ppm) levels of Fe^{2+} in organic solvents.

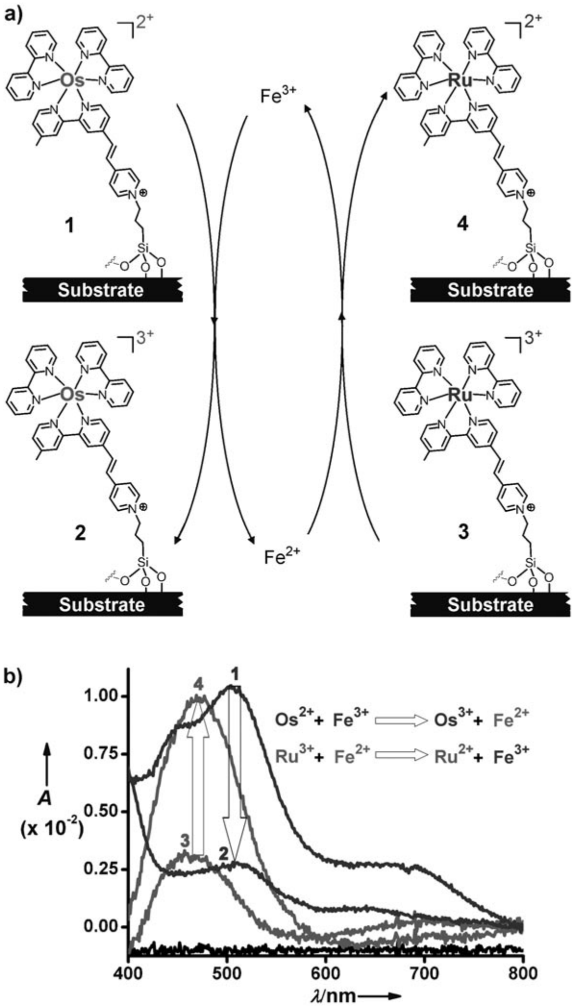

Figure 1. a) Schematic representation of the monolayers (**1**–**4**). b) Representative absorption (UV/Vis) spectra showing the oxidation of Os^{2+}-based monolayers (**1**→**2**) with Fe^{3+} coupled with reduction of the Ru^{3+}-based monolayer (**3**→**4**) in acetonitrile.

Ru^{2+} monolayers (**4**) were activated by immersion of the functionalized glass substrates (0.8 × 2.5 × 0.1 cm) in a 1.0 mM solution of ceric sulphate in doubly distilled water and subsequent rinsing with dry acetonitrile and drying under a

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gentle stream of N_2. Under these conditions, full oxidation of the d^6 metal centers to Ru^{3+} occurred (**4**→**3**) within a three-minute exposure time, as judged optically by bleaching of the characteristic MLCT band at $\lambda = 476$ nm. The original metal oxidation state of the immobilized complexes can be regenerated chemically with Fe^{2+}. For instance, immersion of the activated Ru^{3+} monolayers (**3**) in a dry CH_2Cl_2 solution containing 0.1 ppm $FeCl_2$ for approximately two minutes resulted in full recovery of the optical absorption spectrum of system **4**. Apparently, the monolayers **1**–**4** are redox-active, as also verified by electrochemical measurements on functionalized indium tin oxide (ITO) coated glass. As expected, the ruthenium-based monolayers (**3**, **4**) on ITO substrates exhibit a reversible redox peak (Ru^{2+}/Ru^{3+}) with a half-wave redox potential $E_{1/2} = 1.27$ V versus Pt and 0.90 V versus ferrocene/ferricenium (Fc/Fc^+). Similar behavior has also been observed for the osmium system (**1**, **2**).[29]

Next, a series of experiments was performed to demonstrate chemical communication between the osmium- (**1**) and ruthenium-based monolayers (**3**). In a typical experiment, an Os^{2+}-based monolayer (**1**) on glass was immersed in a dry dichloromethane solution containing 20 ppm $FeCl_3$ and an activated Ru^{3+} monolayer (**4**) on glass. Briefly, the two substrates were fixed in a teflon sample holder and rotated slowly in the solution by magnetic stirring for three minutes. The distance between the surface planes was kept constant at approximately 0.5 cm, which is six orders of magnitude larger than the monolayer thickness of approximately 1.5 nm. Next, both samples were rinsed with dry dichloromethane and acetonitrile and carefully wiped with task paper before recording the optical absorption spectra by standard UV/Vis spectroscopy. The optical characteristics of these monolayers in the visible region before and after the experiment are shown in Figure 1. The optical spectrum of the osmium system is as expected for an oxidation process by Fe^{3+} (**1**→**2**),[28] whereas the optical characteristics of the ruthenium system are typical for the reduction process with Fe^{2+} (**3**→**4**). However, the ruthenium system (**3**) is only reduced in the presence of the osmium-based monolayer in the lower oxidation state (**2**). Various control experiments were carried out as well. For instance, treatment of the Ru^{3+}-based monolayer (**3**) with a dry dichloromethane solution containing 20 ppm $FeCl_3$ did not affect the optical absorbance, whereas dry dichloromethane containing only 0.02 ppm $FeCl_2$ rapidly reduced the system (**3**) to afford monolayer **4**. The oxidation and subsequent reduction processes of the Os^{2+} and Ru^{3+} centers are fully reversible because the setups can be reset with water and 1.0 mM aqueous ceric sulphate, respectively (Figure 2).

It is clear that the oxidation state of one monolayer controls the oxidation state and the optical properties of the other system. However, more information is transferred in this $Fe^{3+/2+}$-mediated process. The optical response of the ruthenium-based monolayer (**3**→**4**) is linear with respect to the dimensions of the glass substrates functionalized with the osmium-based monolayer (**1**) within a given time period, as shown in Figure 3. Full reduction of the Ru^{3+} system (**3**) was achieved within a three-minute exposure time using fourfold larger substrates for the Os^{2+} monolayer (**1**).

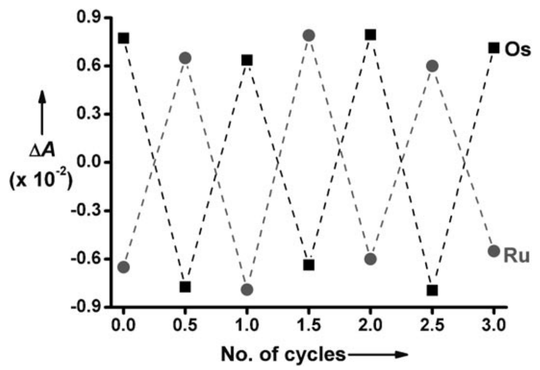

Figure 2. Representative absorption spectral changes of the MLCT bands at $\lambda = 475$ (●, **3**) and $\lambda = 512$ nm (■, **1**) after a communication experiment with $FeCl_3$ in dichloromethane and subsequent chemical recovery with $Ce(SO_4)_2{\cdot}4\,H_2O$ and water for the ruthenium (**4**) and osmium (**2**) systems, respectively.

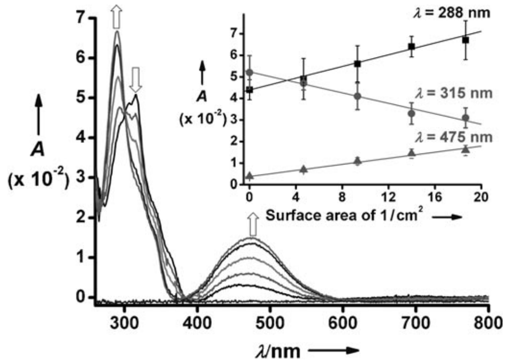

Figure 3. Absorption (UV/Vis) spectra showing the reduction of the Ru^{3+}-based monolayer (**3**) as a function of the surface area of the Os^{2+}-based monolayers (**1**). The surface area of the ruthenium monolayers (**3**, **4**) is maintained constant at 4.7 cm^2. The exposure time was arbitrarily set at 3 min. The inset shows the linear correlations of the spectral changes at various wavelengths versus surface area. The lines are linear fits of the absorption bands at $\lambda = 288$ (■, $R^2 = 0.986$), $\lambda = 315$ (●, $R^2 = 0.976$), and $\lambda = 475$ (▲, $R^2 = 0.992$).

For a communication process using a solution with metal ions to transfer information between two interfaces, it would be expected that the amount of solvent, the information carrier concentration, the distance between substrates, temperature, and so on would play a major role in determining the response time of the system. To verify this expectation, we systematically varied the amount of dichloromethane while maintaining a constant Fe^{3+} concentration and constant substrate dimensions. Indeed, the system response increases by a factor of approximately three upon decreasing the solvent volume from 20 to 5 mL for a three-minute exposure time (Figure 4). The optical deviation from three experiments with the same setup is approximately 12%.

In conclusion, a redox-active monolayer setup has been used to demonstrate information transfer between two interfaces by metal ions as electron carriers coupled with optical readout. This process allows one system to detect the chemical oxidation state and dimensions of other interfaces that are not in direct contact but are placed in the same chemical environment. The response time of the setup is

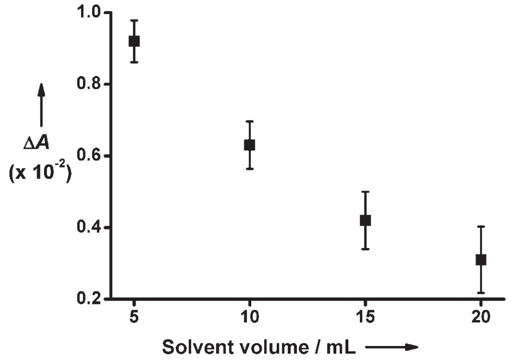

Figure 4. Effect of the amount of dichloromethane on the absorption intensity change at $\lambda = 475$ nm of the ruthenium-based monolayer while keeping the Fe^{3+} concentration (20 ppm) and substrate dimensions ($0.8 \times 2.5 \times 0.1$ cm) constant.

sensitive to the substrate dimensions and the volume of the medium. Importantly, three metals from the same group have been used as a signal generator, information carrier, and reporter system. We believe this model system may evolve into advanced interfacial communication systems based on electrochemically or optically active monolayers.

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