A Monolayer-Based Setup for Optical Amplification

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ABSTRACT Signal amplification has been demonstrated with surface-bound electrochromic complexes that can exist in one of two oxidation states ($M^{2+/3+}$). Reaction of $FeCl_3$ with covalently immobilized Os^{2+} complexes on glass substrates converts the metal centers from one oxidation state to the other. The formed Fe^{2+} reduces a series of Ru^{3+}-based monolayers. The absorption of light is coupled with the oxidation state of the complexes and provides the output for the monolayer-based device. The gain of the setup can be controlled by the addition of a Fe^{2+} chelating ligand.

KEYWORDS: Boolean logic • monolayers • thin films • sensors • communication

Molecular Boolean logic is an elegant way to describe and use changes in the physicochemical properties of a system or material as a result of a specific interaction (e.g., chemical, electrochemical, optical) that can transfer it in a different state (1−4). This concept, introduced in 1993 by de Silva (5), has seen a flurry of activity leading to the design of multitasking compounds (6), bioinspired systems (7−10), and molecular networks (9, 10) capable of mimicking in solution the basic properties of logic gates and circuits (1−4), electronic locks (11, 12), and even calculators (6, 13). The prospect of using (bio)molecules as logic gates and circuits may open a unique route to further miniaturization of central processing units (CPUs) (14). The design of surface confined systems (14−19), integration of logic gates (17, 18, 20), communication (17, 18, 20, 21), and molecular encoding (11, 12, 19) have been explored. In despite of the recent progress, a long difficult road lies ahead with many scientific and engineering challenges. At this stage of fundamental understanding and development of molecular Boolean logic (1−4), demonstration and integration of molecular analogues of essential electronic components and phenomena are needed. This includes the interaction and coupling of different molecular systems. However, one should bear in mind that such molecule-based systems do not always have an existing conventional counterpart, nor it is necessary to exactly reproduce the function and operation of conventional devices. One central component in many devices is the amplifier as it enhances the amplitude of a signal. In this study, we demonstrate that a series of redox-active monolayers have some of the characteristic features of an amplifier: signal enhancement (i.e., gain) and gain control.
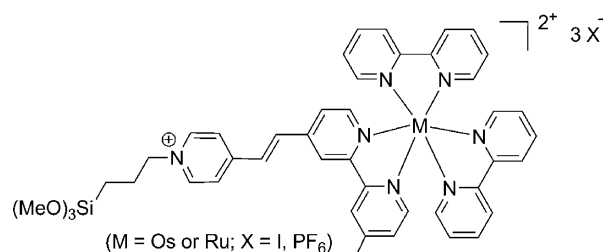
FIGURE 1. Molecular structures of osmium and ruthenium polypyridyl complexes. Monolayers of these robust complexes covalently attached to glass were used as device components in this study (14, 17, 18, 22−25).

We have demonstrated control of the optical properties of monolayer assemblies based on the polypyridyl complexes shown in Figure 1 as a function of their formal metal oxidation state ($M^{2+/3+}$). These monolayer have been fully characterized in our previous reports (14, 17, 18, 22−25). The thermally robust osmium and ruthenium complexes are covalently bound to glass surfaces and can be reversibly oxidized and reduced using common chemical reagents. This monolayer chemistry has been utilized for communication and information transfer between two metal-complex-based interfaces using soluble metal ions ($Fe^{2+/3+}$) as electron carriers (17, 18). Furthermore, we have shown that these redox-active monolayers can be operated as logic gates and mimic the input and output characteristics of electronic circuits when using chemical reagents as inputs and the optical absorption of the system as the output (17). Here, we have extended on these findings by integrating the monolayer assemblies in a new setup that operates like an amplifier.

Our monolayer-based amplifier consists of the aforementioned osmium and ruthenium polypyridyl complexes covalently bound to glass substrates. Metal ion ($Fe^{2+/3+}$) mediated electron-transfer between a series of functionalized substrates immersed in an organic media results in an enhancement of the total optical absorbance of the device by about 1 order of magnitude. Interestingly, the optical gain can be controlled chemically by disrupting the electron flow
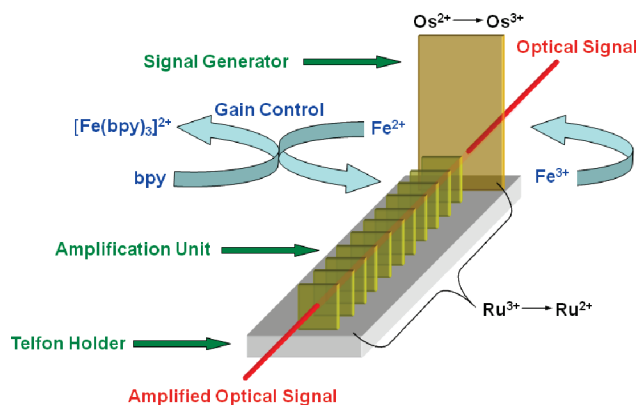
FIGURE 2. Schematic of the setup used for the optical amplification. The amplification unit consists of a series of twenty glass slides (total surface area ≈ 80 cm^2) functionalized with a covalently bound Ru^{3+}-based monolayer. The initial optical signal is generated by an analogous Os^{2+}-based monolayer placed in parallel to the Ru^{3+}-functionalized slides. Additional slides functionalized with the Os^{2+}-based monolayer were placed in the same reactor with a total surface area ≈ 184 cm^2. The planes of the glass substrates are placed parallel to each other separated by 0.2 cm in a custom-built Telfon sample holder. The experiments were performed using dry acetonitrile as the solvent with 20 ppm of FeCl$_3$ as the input. The solution was stirred during the experiments. The optical measurements were performed ex situ. A series of Ru^{3+}-based monolayers and one blank glass substrate were used for background correction. The figure is not drawn to scale and only 12 slides are shown.

between the different monolayers. The addition of a chelating ligand (bipyridyl) to the system traps the metal ions that act as electron carriers and thus disrupts the communication between the interfaces. A schematic drawing of our experimental setup for the signal amplification system is shown in Figure 2.

In the experimental setup described here, we first recorded the optical spectrum in the transmission mode of the Os^{2+}- and Ru^{3+}-based monolayers by placing all the slides parallel to each other in one Telfon sample holder. A series of Ru^{3+}-based monolayers and one uncoated glass slide was used for background correction resulting in the absorption spectrum of the Os^{2+}-based monolayer (Figure 3A, purple line a). Subsequent treatment of the system with a dry acetonitrile solution containing 20 ppm of FeCl$_3$ for 5−7 min followed by ex situ UV/vis measurements showed the presence of the MLCT band of the Ru^{2+}-system at $\lambda = 467$ nm that is about one magnitude of order stronger than the input signal at $\lambda = 516$ nm (Figure 3A, lines a and d). These significant optical changes indicate that the Fe^{2+} formed by reduction of Fe^{3+} by the Os^{2+}-based monolayer reacted with the series of Ru^{3+}-based monolayers. These surface-bound Ru^{3+} polypyridyl complexes do not react with FeCl$_3$, but are readily reduced with sub-ppm levels of FeCl$_2$ (17, 18). The monolayer-based amplifier can be reset by washing the Os^{3+}- and Ru^{2+}-functionalized elements separately for a few minutes with water (17, 18, 22−25) and with an aqueous Ce^{4+} salt solution, respectively (17, 18).

The output of a device is generally capable to drive only a limited number of other systems (i.e., fan-out behavior). Such a limit is not observed here as the entire amplification unit has been fully addressed. All the Ru^{3+}-based monolayers were reduced as determined by UV/vis mea-
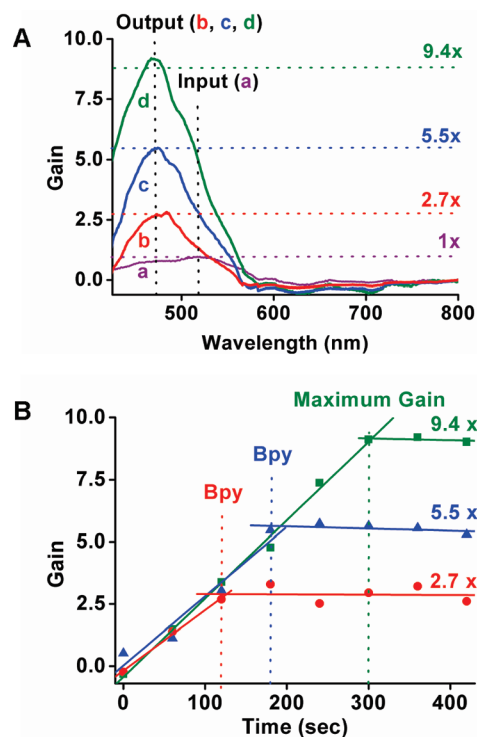
FIGURE 3. Optical amplification experiment and gain control. (A) Representative combined absorption spectra of 20 Ru-based monolayers (amplification unit) addressed by the Fe^{2+} (signal carrier) that was generated from the in situ reduction of Fe^{3+} (20 ppm) by the reaction with the Os^{2+}-based monolayer (signal generator). (a) Purple line, Os^{2+}-based monolayer with $\lambda_{input} = 516$ nm at $t = 0$ s; (b) red line, mixed Ru$^{2+/3+}$-based monolayers after addition excess of bpy (100 ppm) at $t = 120$ s; (c) blue line, mixed Ru$^{2+/3+}$-based monolayers after addition excess of bpy (100 ppm) at $t = 180$ s; (d) green line, Ru^{3+}-based monolayers at $t = 300$ s. B) Corresponding UV/vis follow-up experiments demonstrating the gain control by trapping of the Fe^{2+} by addition of excess bpy to the system. The red, blue and green lines are linear fits with $R^2 > 0.98$ and serve as guides to the eye after reaching the maximum gain. For both a and b, the absorption intensities at $\lambda_{out} = 467$ nm were used to monitor ex situ the signal amplification. Twenty Ru^{3+}-based monolayers on glass substrates and one glass substrate were used for background correction. All experiments have been performed at least three times and the experimental error is <15%.

surements of each individual slide. Indeed, longer reaction times did not improve the optical gain. Therefore, the maximum observed gain ($I_{output}/I_{input} = 9.4$) should be as high as the experimentally achievable absorption for twenty Ru^{2+}-functionalized slides divided by the absorption intensity of the Os^{2+}-based monolayer. In fact, the amplification is very efficient, and the experimentally observed gain of the monolayer-based optical amplifier is close to the maximum possible value: The output signal intensity is ~80% of the combined absorption of a set of twenty Ru^{2+}-based slides (see Figure S1 in the Supporting Information). The difference is caused by the series of twenty Ru^{3+}-based slides used for baseline correction in our device setup. Their absorption lowers somewhat the maximum possible gain by ~20%. Regular amplifiers often exhibit a nonlinear gain and such behavior is observed here as well. The absorption intensities of the surface-confined Ru^{2+}- and Os^{2+}-based complexes at these wavelengths are very similar. However, the gain does not scale linear with

the number of glass slides coated with the Ru^{3+}-based monolayers because of light scattering. Measuring the optical absorption at $\lambda = 467$ nm as a function of the number of functionalized glass substrates reveals that the absorption intensity does not increase by a factor of 2 upon doubling the number of slides within the range of 0–24 slides and actually levels off.

We also demonstrate here molecular-based gain control using the same setup shown in Figure 2 by adding at a given time an excess of an Fe^{2+}-chelating ligand to the solution to disrupt the electron-flow to the series of Ru^{3+}-based monolayers. Previous studies by us (24) showed that Fe^{2+} generated by a redox reaction between the Os^{2+}-based monolayer and $FeCl_3$ can be trapped by 2,2′-bipyridyl (bpy) to afford $[Fe(bpy)_3]^{2+}$. The latter compound was observed by UV/vis measurements and mass spectrometry. The solution-to-surface electron-transfer between Fe^{2+}- and the Ru^{3+}-based monolayer is much faster than the reaction between $[Fe(bpy)_3]^{2+}$ and the same interface. Therefore, we succeeded in the current experimental setup to decrease the maximum observed gain at $\lambda = 467$ nm from 9.4× to 5.5× or 2.7× by the addition of a 5-fold excess of bpy to the $FeCl_3$ containing solution of our amplifier, 3 or 2 min, respectively, after the addition of the metal salt (Figure 3B). A good amplifier should cause signal enhancement with as little signal distortion as possible. In our case, the maximum amplified signal mimics the input signal but is blue-shifted by about 47 nm. Statistically, this output signal matches well with the original spectrum as indicated by the correlation coefficient, $R^2 = 0.91$, for an optical window of 75 nm after correcting for the inherent shift in peak position. This shift is due to the use of the two different metals (Os vs Ru). Furthermore, the system exhibits linear behavior and plotting time versus gain gives a correlation with $R^2 > 0.98$ (Figure 3B).

Several organic materials capable of optical amplification including metal complexes (26), monolayers (27), and polymers (28) are known. The hereinabove described experimental setup combines interfacial communication by means of electron-transfer with a controllable gain of the amplified optical output. Although the presented system is large and relative slow, its overall behavior resemblances some of the properties of conventional amplifiers. However, one should take into consideration that the description of molecular-based systems in terms of existing electronic units is a matter of convenience as both systems operate in a fundamentally different way, but their input and output characteristics do have some resemblance. The use of electrochemical methods and/or light as inputs is expected to significantly enhance the device performance (29, 30). The components used to build this monolayer-based device can be operated as sensors (22−25) or logic gates and mimic the properties of electronic circuits (14, 17, 18). For instance, it is possible to selectively and accurately detect and quantify parts-per-million (ppm) levels of Cr^{6+} in H_2O (22), H_2O (23), and Fe^{3+} in various solvents (24) and NO_x in air (25) with the $Os^{2+/3+}$-based monolayers. Integration of one of the

above-mentioned functions with the presented monolayer-based optical amplifier using microfluidics (31) might be realistically possibility. The nanoscale monolayers are able to control the optical properties of a straightforward device that is magnitudes of order larger. These observations might be a new entry to the design of thin-film-based machinery and devices (32−34).

Supporting Information Available: Experimental procedures and Figure S1 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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