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Molecular and Biomolecular Assemblies Based on Photochromic Compounds

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Photoswitchable redox-activated monolayers on electrode supports act as molecular electronic systems for the electronic transduction of recorded photonic information. Photoisomerizable monolayers assembled on electrodes may act as command interfaces for controlling interfacial electron transfer and thus act as interfaces for the amperometric transduction of photonic signals recorded by the monolayer. Photoswitchable biomaterials assembled on electronic transducers represent novel optobioelectronic systems. This is exemplified by the organization of a photoswitchable enzyme for the amplified amperometric transduction of photonic signals, and by the tailoring of reversible immunosensor systems.

Keywords: Molecular switches; photoswitch; Biomaterial photoswitches; Optobioelectronics; Monolayers; Immunosensors

The integration of photoswitchable molecular and biomolecular components with electronic transducers provides a means to tailor molecular optoelectronic [1] and optobioelectronic systems [2]. The present paper addresses several concepts that were developed by us to assemble molecular and biomolecular optoelectronic systems. We discuss methods to organize systems that lead to the electronic transduction of photonic signals recorded by the array, and exemplify the use of photoisomerizable interfaces as functional arrays that control interfacial electron transfer or act as reusable sensing interfaces.

Figure 1 outlines two concepts to nano-engineer electronic transducers with photoswitchable molecular monolayers that lead to integrated molecular electronic systems for the reversible electronic

transduction of recorded photonic information. By one approach, Figure 1(A), the photoisomerization activates redox-functions of the monolayer array. While one state of the monolayer, State A, does not exhibit redox functions, and represents an "OFF" state lacking electrical contact with the electrode, photoisomerization to state B activates redox-functions of the interface, and the photochemical transformation occurring on the surface is transduced as an amperometric output. By the reversible photoisomerization of the monolayer between states A and B the system is cycled between "OFF" and "ON" redox-states, respectively. The second method to tailor integrated systems for the electronic transduction of photonic signals is exemplified in Figure 1(B), and involves the organization of a photoisomerizable layer on a transducer acting as a "command interface" for controlling interfacial electron transfer.

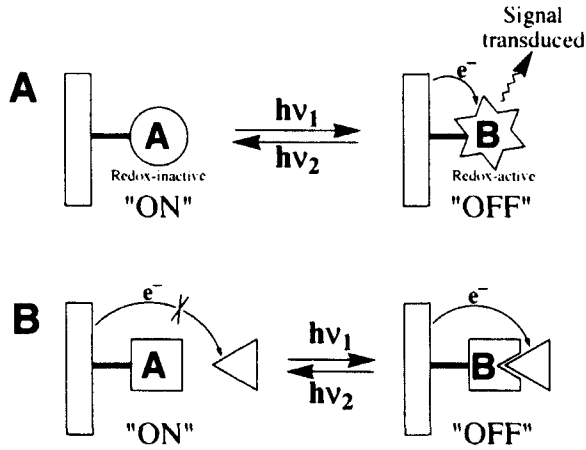

FIGURE 1. Methods to assemble photoswitchable molecular assemblies acting as electronic devices: (A) Design of a photochemically redox-activated monolayer-electrode. (B) The organization of a photoisomerizable command interface that controls interfacial electron transfer.

Figure 2(A) shows the assembly of the photoisomerizable phenoxynaphthacene quinone monolayer on an Au-electrode. In the "*trans*" quinone state, the monolayer exhibits quasi-reversible redox properties, Figure 2(B), curve (a). Photoisomerization of the monolayer to the "*ana*"-quinone state yields a redox-inactive monolayer interface, and only the background current of the electrolyte solution is observed,

Figure 2(B), curve (b). By the cyclic photoisomerization of the monolayer interface between the "*trans*" and "*ana*" states, reversible "ON" and "OFF" electrochemical switching of the nano-engineered surface is feasible (inset, Figure 2(B)). This enables the amperometric transduction of recorded photonic information, the erasure of the recorded information, and the reactivation of the photosensitive interface [3].

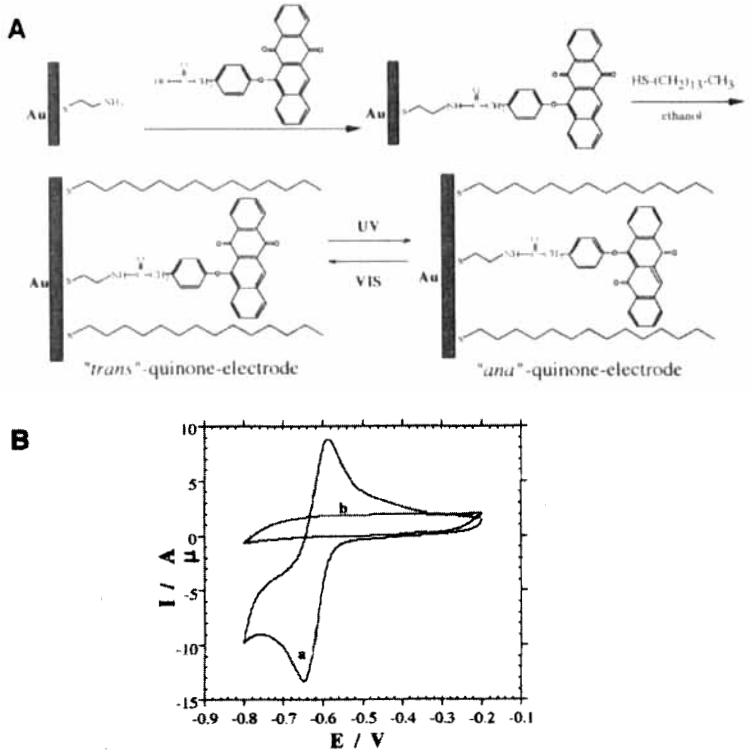

FIGURE 2. (A) Assembly of a photoisomerizable, redox-activated, monolayer on an Au-electrode. (B) Cyclic voltammograms of the photoisomerizable electrode: (a) In the "*trans*" quinone state. (b) In the "*ana*" quinone state. Measurements in 0.01 M phosphate buffer, pH=7.0 and 0.1 M Na_2SO_4, scan rate 50 $mV \cdot s^{-1}$. Inset: Cyclic amperometric transduction of the photoisomerization occurring on the electrode.

Figure 3(A) shows the assembly of the photoisomerizable nitrospiropyran monolayer, (**1a**), on an electrode support. The monolayer-functionalized-electrode acts as a "command interface" for controlling the interfacial electron transfer by external light-triggering signals and for the electrochemical transduction of recorded photonic information, Figure 3(B), [4]. At the nitrospiropyran-functionalized electrode, the electrochemical oxidation of dopamine proceeds effectively, Figure 3(B), curve (a). Photoisomerization of the monolayer to the protonated nitromerocyanine state, (**1b**), results in the electrostatic repulsion of the positively-charged redox-probe dopamine (**2**). The electrostatic repulsion of (**2**) introduces a kinetic barrier for the oxidation of (**2**), as evident by its inefficient oxidation, Figure 3(B), curve (b). By the cyclic photoisomerization of the monolayer between the (**1a**) and (**1b**) states, the interfacial electron transfer can be switched reversibly between the "ON" and "OFF" states (inset, Figure 3(B)).

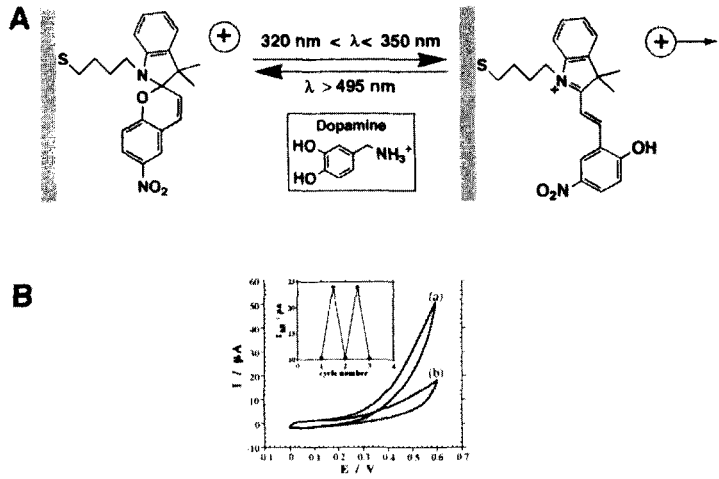

FIGURE 3. (A) The assembly of a reversible nitrospiropyran photoisomerizable monolayer on an Au-electrode. (B) Cyclic voltammograms corresponding to the oxidation of dopamine, (**2**): (a) At the protonated nitromerocyanine-functionalized electrode. (b) At the nitrospiropyran-functionalized electrode. Inset: Cyclic amperometric transduction of photonic signals recorded by the monolayer through the electrochemical oxidation of (**2**). Data recorded in 0.02 phosphate buffer pH=7.0, scan-rate 200 $mV \cdot s^{-1}$.

Photoswitchable activation and deactivation of redox-enzymes enables the amplified bioelectrocatalytic transduction of recorded optical signals [2]. Previous methods to photoregulate the bioelectrocatalytic functions of redox-enzymes included the assembly of enzymes tethered with photoisomerizable units on electrodes [5] and the reconstitution of apo-enzymes with photoisomerizable cofactor units [6]. Recently, we developed a novel method to tailor a photoswitchable bioelectrocatalytic system by the assembly of a "smart" biocatalytic interface on an electrode. Figure 4(A) shows the assembly of the "smart" bioelectrocatalaytic layer on the electrode. A mixed monolayer consisting of an FAD cofactor, covalently-tethered to a lipoic acid monolayer, and of a nitrospiropyran monolayer, was assembled on an Au-electrode, [7]. The apo-glucose oxidase was reconstituted onto the FAD-cofactor sites to yield an aligned photoisomerizable enzyme layer. Electrical contacting of the redox-enzyme and the electrode was established by the application of N,N-dimethyl-2-ethylammonium ferrocene, (**3**), as positively-charged diffusional electron relay. In the presence of the monolayer consisting of the nitrospiropyran state, the positively-charged diffusional relay mediates the electron transfer between the enzyme redox-site and the electrode, a process that activates the bioelectrocatalytic oxidation of glucose to gluconic acid, Figure 4(B), curve (b). Photoisomerization of the composite monolayer to the positively-charged protonated nitromerocyanine state, inhibits the bioelectrocatalytic oxidation of glucose, Figure 4(B), curve (c). Blocking of the bioelectrocatalyzed oxidation of glucose originates from the electrostatic repulsion of the electron mediator by the positively-charged units of the protonated nitromerocyanine sites that act as a command interface that controls the electrical contact between the enzyme and the electrode. By the reversible photoisomerization of the composite monolayer between the nitrospiropyran state, SP-state, and the protonated nitromerocyanine state, MRH^+-state, the bioelectrocatalytic function of the enzyme layer is reversibly-switched between "ON" and "OFF" states, respectively, Figure 4(B), inset

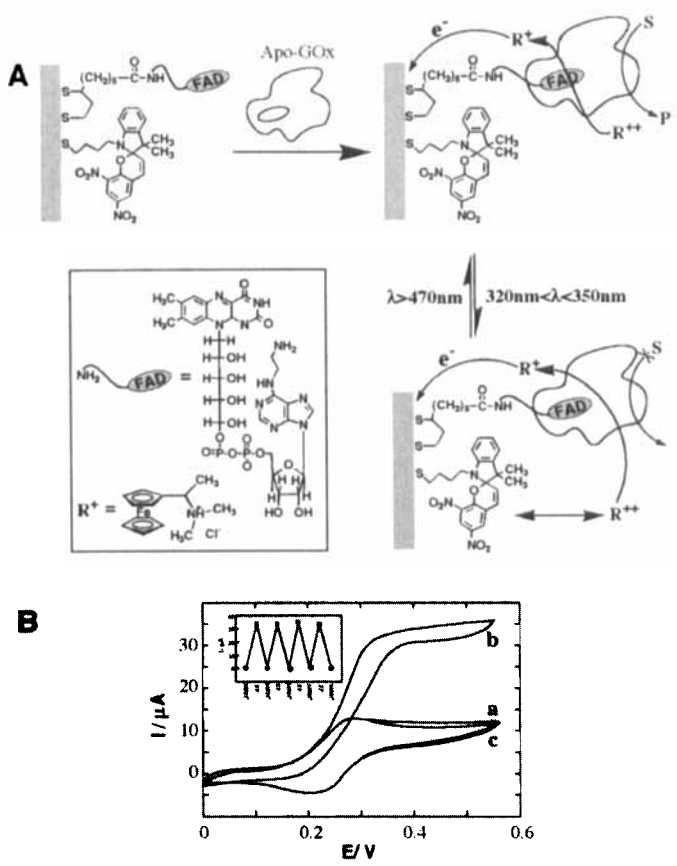

FIGURE 4. (A) Assembly of a mixed monolayer consisting of FAD and nitrospiropyran photoisomerizable units on an Au-electrode. (B) Reconstitution of apo-glucose oxidase on the mixed FAD/nitrospiropyran monolayer. (C) Photoactivation of the enzyme monolayer in the presence of (3), 5×10^{-4} M, as diffusional electron mediator: (a) In the presence of the nitrospiropyran monolayer electrode without glucose. (b) In the presence of the nitrospiropyran monolayer-electrode and glucose, 1×10^{-2} M. (c) In the presence of the protonated nitromerocyanine electrode and glucose, 1×10^{-2} M. Measurements in phosphate buffer, 0.1 M, pH=7.0, 37°C, scan-rate 4 $mV \cdot s^{-1}$. Inset: Cyclic amperometric transduction of the photonic activation of the bioelectrocatalytic electrode through the oxidation of glucose.

Photoswitching of the functions of biomaterials may be directed to the light-controlled affinity interactions of biomaterials with their complementary components [8]. The photoregulation of antigen-antibody interactions represents one class of photoswitchable affinity interactions that may lead to the development of reversible immunosensors, Figure 5(A). In state A of the monolayer, the interface binds the antibody, and the formation of the affinity complex on the surface is transduced to the macroscopic environment. This process represents the sensing event of the antibody. Photoisomerization of the monolayer to state B generates an interface that lacks antigen properties. This enables washing-off the antibody and, by a second illumination cycle, the sensing interface in state A can be regenerated. Thus, by the application of a photoisomerizable antigen monolayer on an appropriate transducer, sensing of an antibody followed by the regeneration of the immunosensor is feasible, and a route to design reusable immunosensors is established. Following this concept, the cyclic sensing of the anti-dinitrophenyl antibody, DNP-Ab was demonstrated [9]. A dinitrospiropyran monolayer was assembled on an Au-support, Figure 5(B). The dinitrospiropyran monolayer acts as antigen for the DNP-Ab. Binding of the antibody to the surface may be transduced by amperometric signals [9], microgravimetric, quartz-crystal-microbalance, assay [9], Faradaic impedance spectroscopy [10] and Surface Plasmon Resonance, SPR, [11]. The photoisomerization of the monolayer to the protonated dinitromerocyanine generates an interface that lacks antigen properties for the DNP-Ab. This allows washing-off the antibody and regenerating the active dinitrospiropyran layer by a second illumination cycle. Thus, by a two-step irradiation process, the sensing interface can be regenerated for the reversible analysis of the antibody. Figure 5(C) and Figure 5(D) illustrate the cyclic sensing of the DNP-Ab using Faradaic impedance spectroscopy and SPR, respectively. Binding of the DNP-Ab to the dinitrospiropyran monolayer results in the insulation of the electrode and an enhanced interfacial electron transfer resistance, R_{et}, is observed in the impedance spectrum. Similarly, association of the DNP antibody on an Au/glass support alters the thickness and refractive index of the modifying interface, resulting in a shift in the minimum reflectivity angle in the SPR spectrum.

In conclusion, the report has addressed novel means to organize molecular and biomolecular photoswitches. These systems open new perspectives in tailoring molecular and biomolecular optoelectronic systems.

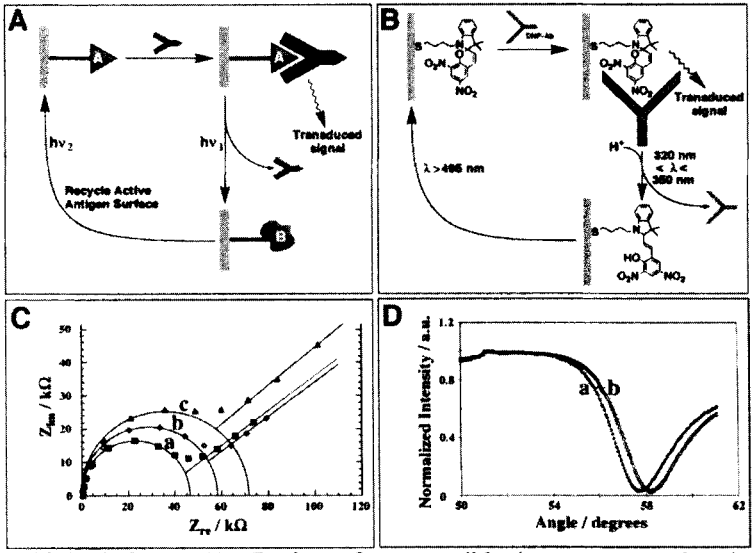

FIGURE 5. (A) Design of a reversible immunosensor by the application of a photoisomerizable antigen monolayer on a transducer. (B) Reversible sensing of the DNP-Ab by a photoisomerizable dinitrospiropyran monolayer-electrode. (C) Cyclic sensing of the DNP-Ab by Faradaic Impedance Transduction. (D) Surface Plasmon Resonance analysis of the reversible binding and dissociation of DNP-Ab to and from the photoisomerizable interface.

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