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Short communication

Surface plasmon resonance study on the interaction of photochromic spironaphthoxazine with L-phenylalanine in self-assembled monolayers on gold

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Abstract

We report evidence of photoisomerization-induced complexation with L-phenylalanine in the thin film of spironaphthoxazine (SNO)–alkanethiol self-assembled monolayer by surface plasmon resonance (SPR). The betainic nature of merocyanine give rise to simultaneous binding of the positively changed ammonium group and anionic carboxylate function of L-phenylalanine under UV irradiation. SPR revealed that increased L-phenylalanine concentration afforded an increase in the relative resonance angle shift.

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Application of light-stimulated photorecognizable substances as reversible image recording and bioelectronic materials is a subject of extensive research effort [1]. Spironaphthoxazines are photochromic compounds analogous to spiropyrans. These two classes of compound are similar in many respects. However, the replacement of the benzopyran ring by a naphthoxazine ring result in spironaphthoxazine having the advantage of greatly improved resistance to prolonged UV irradiation, which confers a much more commercial importance of them [2]. On UV irradiation the C–O bond of the colorless spironaphthoxazine is cleaved and the colored merocyanine form is obtained.

Thus, the interconversion of spiro (SP)–merocyanine (MC) systems, SP–MC, has been extensively investigated due to their potential applications in molecular devices and uses in biotechnology [3]. It has been reported that spiropyrans and spironaphthoxazines, which possess a coordinating group next to the O atom, can act as chelating agents in the colored open form [4]. In the field of molecular recognition of organic compounds, much interest has been focused on amino acids as an important class of biomolecules.

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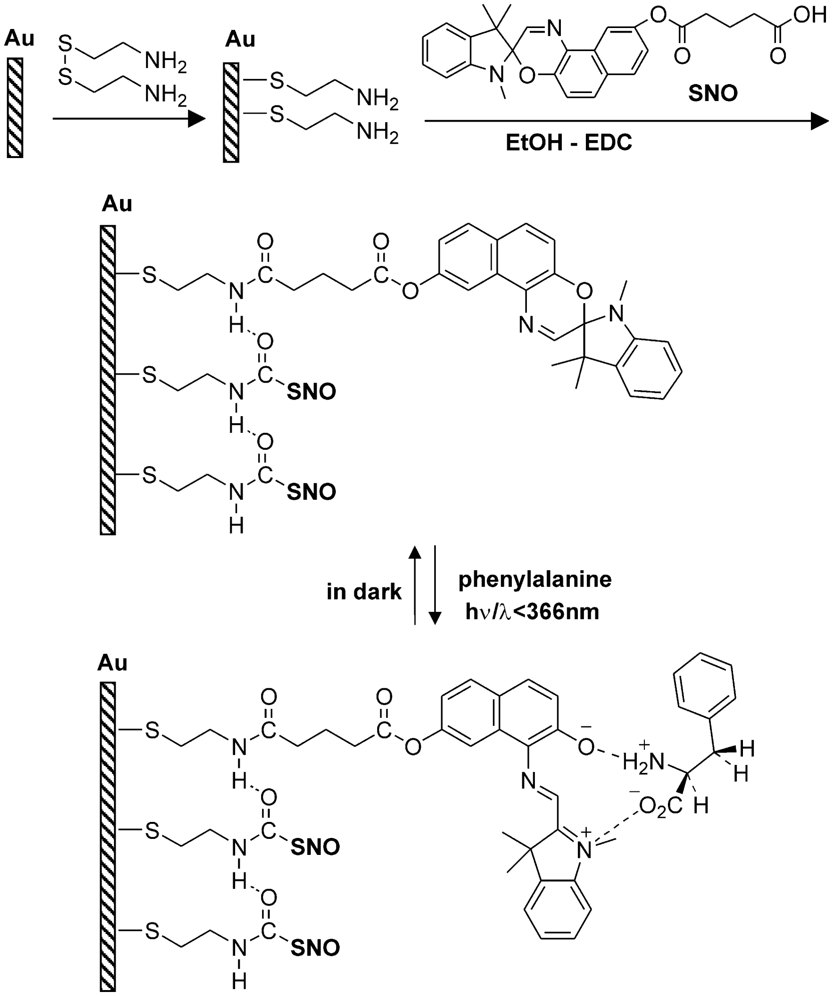
To our knowledge, there are no published accounts of photoinduced amino acid complexation by spironaphthoxazines (SO). We have previously reported the synthesis and self-assembly of the photochromic SO containing alkanethiol with an amide group incorporated into the backbone [5]. The FTIR-RAS shows strong NH stretching (amide A) at 3163 cm^{-1}, C=O stretching (amide I) at 1668 cm^{-1} and NH in-plane bending (amide II) at 1539 cm^{-1} [5(b)].

Here we describe the interaction of amino acid such as L-phenylalanine with SO in a SAM using surface plasmon resonance (SPR) spectroscopy. A monolayer was assembled on Au as outlined in Scheme 1.

In the course of our studies on the design of photochromic SAM, we have observed that a newly reported SNO [6] is highly suited for this purpose. A cyatamine monolayer was first assembled on Au. SNO was coupled to the base monolayer using a small amount of 1-ethyl-3-(3-(dimethylamino)propyl)-carboimide (EDC) as recently derscribed [7].

The mean value of the heights from the cross-sectional analysis of bare gold, the surface roughness, *R*q, is about 24.9 Å [Fig. 1(1)]. The surface

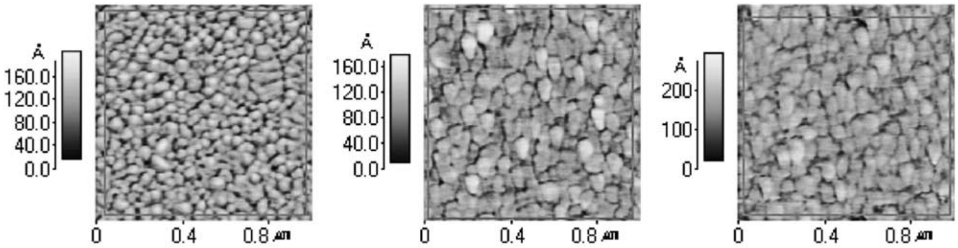


Scheme 1. Stepwise organization of a spironaphthoxazine monolayer on Au.

roughness of cystamine deposited surface on the gold surface, *R*q, is 21.7 Å [Fig. 1(2)]. The SAM film of the spiroxazine–cystamine–gold is composed of much greater grain size. Its surface roughness is 30.0 Å [Fig. 1(3)]. This increased surface roughness arises from the stepwise chemical assembly.

The time-resolved SPR measurement of the formation of a SNO SAM is shown in Fig. 2. The resonance angle is given as a function of time. The increase in the resonance angle indicates formation of a SAM. The molecular structure of open form SO provide two binding sites such as indolenine cation and oxazinic O^-. The betainic nature of MC give rise to simultaneous binding of the positively charged ammonium group and anionic carboxylate function of amino acids. Pioneering studies of amino acid recognition include the transport of L-phenylalanine through a liposomal bilayer by a merocyanine dye as a photoswitchable carrier [8].

Fig. 3 shows the resonance angle shift for SAM of photochromic SNO before and after exposure to UV ($\lambda < 366$ nm) irradiation under different L-phenylalanine concentrations where θ is the resonance angle before irradiation, $\Delta\theta$ is the resonance angle shift at any time after irradiation.



(1) (2) (3)

Fig. 1. Atomic force microscope images of the film surface: (1) bare gold; (2) cystamine–gold, (3) SNO dye–cystamine-gold.

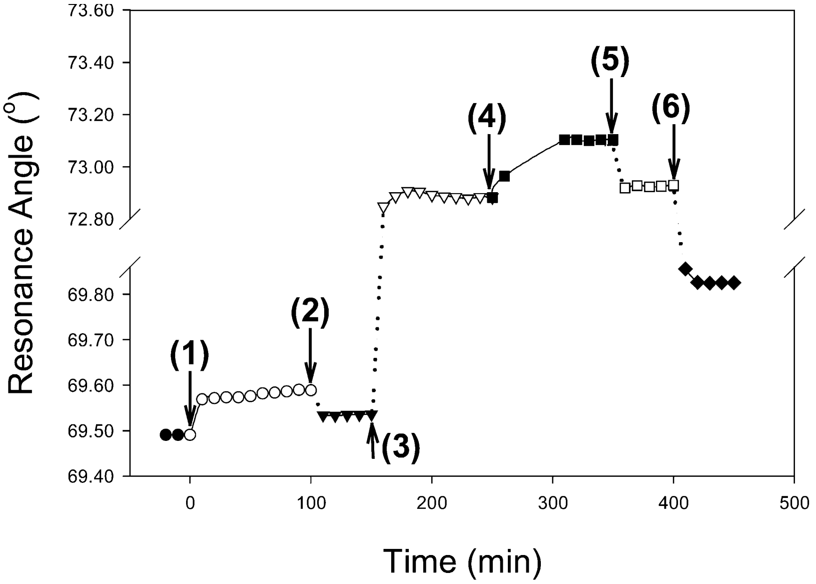


Fig. 2. Monitoring of the formation of a spironaphthoxazine SAM. Resonance angle as a function of time: (1) injection of cystamine solution (0.01 M) in water; (2) washing with water; (3) washing with EtOH; (4) formation of amide bond with a mixture of SNO (5×10^{-4} M) and EDC (0.01 M) in EtOH; (5) washing with EtOH; (6) washing with water.

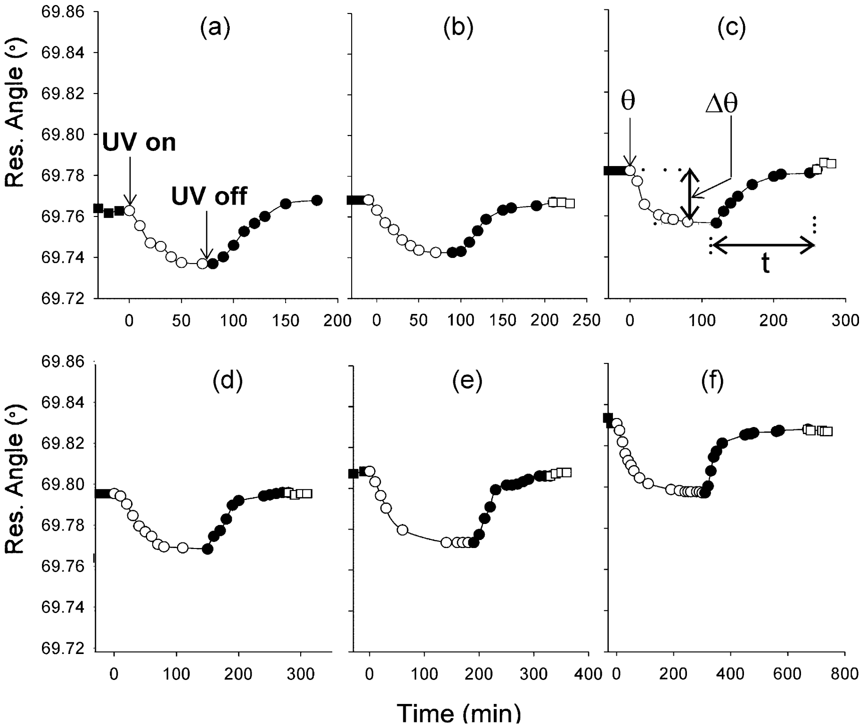


Fig. 3. Resonance angle shift on SAM according to various L-phenylalanine concentrations before and after UV irradiation: (a) buffer solution; (b) 10^{-14} M; (c) 10^{-12} M; (d) 10^{-10} M; (e) 10^{-8} M; (f) 10^{-6} M, pH 6 with 0.05 M phosphate buffer.

The complexation properties of SNO to L-phenylalanine were studied in buffer solution (pH 6, 0.05 M phosphate buffer). The most widely used methods of exciting surface plasmons are based on the evanescent wave excitation using a Kretschmann prism configuration [9].

In these methods, a *p*-polarized laser beam (4.5 mW. 675 nm) in incident upon the metal-prism interface and the reflected beam is detected by photodiode. Its signal is recorded with an optical power meter (ANDO Electric Co. Ltd., AQ1135E). When the incident angle reaches an appropriate value, the reflection decreases sharply to a minimum (i.e. surface plasmon is resonantly excited at this angle). The incident angle is controlled using a stepping moter with a 0.002° of minimum resolution. A high-pressure mercury lamp (Ushio, SP3-250D) was used as the UV radiation source and was calibrated with UV filter.

After having injected the various concentrations of sample solution, we measured the resonance angle when it remained unchanged. And then the SAM was washed several times with buffer solution and repeated the measurement. The re-measured resonance angles did not return to its original value in buffer solution. It mostly keeps a higher resonance angle than the original resonance angle.

It is considered that there is a memory effect from remaining of betainic phenylalanines in SAM. In the SPR method, the resonance angle is very sensitive to variation of the medium outside the metal film. The observed resonance angle shift induced by UV irradiation can be rationalized by the formation of the photoinduced ring opened MC form. These observations may suggest that the influence of the betainic L-phenylalanine on the complexation of photocolored state of SNO could be illustrate in Scheme 1. Such photocomplexation and decomplexation cycles could be repeated many times.

Fig. 4 shows the changes in relative resonance angles induced by UV irradiation by added various concentration of L-phenylalanine. It is clear that increased L-phenylalanine concentration afforded an increase in the relative resonance angles shift.

Thermal relaxation time in going from the MC to the SP forms which correspond to the decomplexation process increases with increasing concentration of L-phenylalanine (Fig. 5).

The prominent feature of the photochromic complexation was significant retardation of the thermal decomplexation. The reason why the rise time is longer than the fall time is explained that quantum efficiency of the reversal process is lower than that of forward case like a previously reported study [10]. Owing to complexation at trace levels and a response to L-phenylalanine, spironaphthoxazine SAM appears to be suitable for practical SPR sensor application.

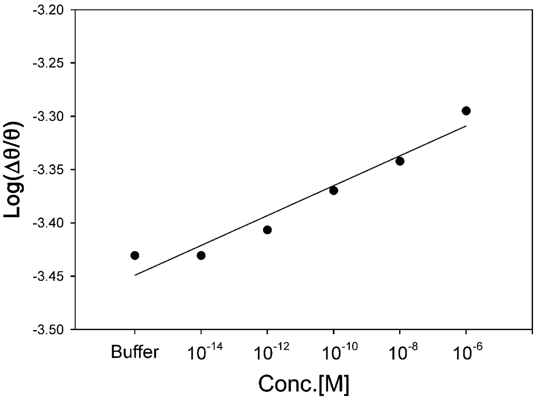


Fig. 4. Relative resonance angle shift of SAM upon UV irradiation at various concentration of L-phenylalanine.

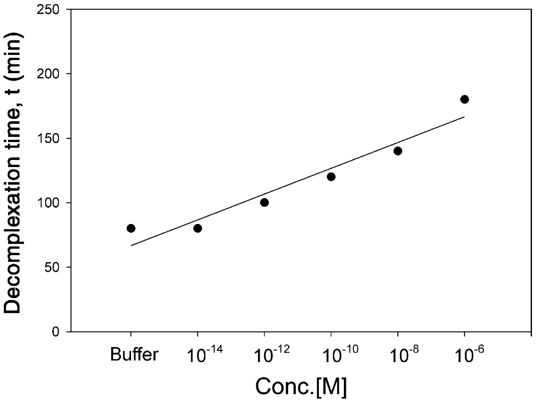


Fig. 5. Dependence of the decomplexation time on concentration of L-phenylalanine with SPR system.

Acknowledgements

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[6] All analytical data agree with the proposed structure for SNO:MP: 188–191 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): $\delta = 8.22$ (1H, d, $J = 2.2$ Hz), 7.75 (1H, d, $J = 8.8$ Hz), 7.22 (1H, d, $J = 8.9$ Hz), 7.65 (1H, d, $J = 8.9$ Hz), 7.22 (1H, d, $J = 8.9$ Hz), 7.13 (2H, m), 6.98 (1H, d, $J = 8.8$ Hz), 6.90 (1H, m), 6.58 (1H, d, $J = 4.8$ Hz), 2.76 (5H, m), 2.58 (2H, t, $J = 7.2$ Hz), 2.14 (2H, m), 1.35 (3H, s), 1.34 (3H, s); anal. found: C, 70.39; H, 5.80; N, 5.92%. Calcd for $C_{27}H_{26}N_2O_5$: C, 70.73; H, 5.72; N, 6.11%.

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