Self-assembled Monolayers of Spironaphthoxazine–Thioether for UV-controlled Complexation

Huan Chen,[††] Yapeng Li,[††] Fengwei Huo,[††] Zhiqiang Wang,*[†] and Xi Zhang[†,††]
[†]*Department of Chemistry, Tsinghua University, Beijing, 100084, P. R. China*
[††]*Key Laboratory for Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130023, P. R. China*

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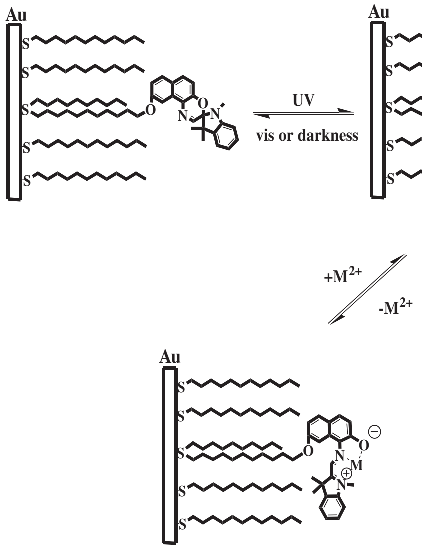
We have demonstrated that the self-assembled monolayer (SAM) of spironaphthoxazine-thioether (SNOTE) can complex metal ions based on the complexation property of the open ring form of spironaphthoxazine induced by UV irradiation, and the well-isolated sensing species in SAMs show a kinetic advantage over the closely packed ones.

Spiropyran/spirooxazine is a type of well-known photo-isomeric molecules for potential applications in optical switching, memory, and sensors.[1] Once exposed under UV light, the single C–O bond in the pyran or oxazine ring can be cleaved, which results in a relatively more polar species (merocyanine form). The whole process can be reversed by visible light or just being put into darkness. The electron-rich oxygen atom in the merocyanine form can complex metal ions. Buncel et al.[2] have studied the thermally stable spiropyran–merocyanine photoswitch in solution that is modulated by the metal cations $Ca^{2+}$and Zn^{2+}. In our previous work,[3] we have synthesized a dendrimer bearing spironaphthoxazine groups on its periphery, which can act as a carrier of metal ions that can be chelated and released by a light beam.

Since the pioneer work of Nuzzo[4] and Sagiv[5] et al., self-assembled monolayers (SAMs) have been proved as a convenient way to produce surfaces with specific chemical functionalities that allow the precise tuning of surface properties. They have been used in lubrication, in corrosion protection, as photolithograpical or electrical resists, and in sensing.[6] In this letter, we report the attempt to combine the photo-driven conformational change and the surface engineering, and demonstrate the difference of the kinetic behaviors between the two kinds of SAMs, the pure SNOTE SAM, and the SAM with thinner-molecules (see Scheme 1). We would expect that the well-isolated sensing species in SAMs may show kinetic advantage over the closely packed ones.



Scheme 1. Self-assembled monolayer containing spironaphthoxazine-thioether (SNOTE) can detect metal ions based on the complexation property of the open ring form of spironaphthoxazine upon UV irradiation.

The SNOTE was synthesized by adding dropwise 5.91 g of 11-bromoundecyl decyl sulfide (30 mL of dry DMF solution) to a mixture of 5.00 g of spironaphthoxzine and 0.30 g of NaH in 70 mL dry DMF. The mixed solution was stirred for 48 h shielded in the darkness and protected by nitrogen. After removing the solvent by vacuum, the resulting mixture was dissolved in dichloromethane to filter out the sodium salt of spironaphthoxazine. The crude product was gained by column chromatography. Recrystallization was performed in ethanol to obtain pure product.[7]

SAMs of SNOTE were prepared by dipping the gold-coated quartz slides into the corresponding 1 mM THF solution at room temperature. After 24 h, the SNOTE modified substrates were rinsed with pure THF, and dried under a nitrogen stream. For the sake of UV-controlled experiment, the SAMs were immersed in Zn^{2+} (0.1 mM) aqueous solution for different time under irradiation of UV optical fiber source. The SNOTE and dodecanetiol (SC_{12}) co-assembled monolayers were prepared by immersing the gold substrates into the corresponding THF solution (1 mM, $SNOTE/SC_{12} = 1{:}1$ molar ratio) for 24 h, and were then subjected to the same rinsing procedure as described above. Before complexation, the spectral intensity of the pure SNOTE or SNOTE/SC_{12} SAMs is rather lower to justify a monolayer coverage.

UV–vis spectroscopy was used to follow the complexation process of SAMs of pure SNOTE on gold substrates, which were immersed in Zn^{2+} aqueous solution under UV irradiation. From Figure 1a, we can clearly see that the absorbance around 480 nm increases gradually with immersed time. The absorbance around 480 nm is ascribed to the complexation between Zn^{2+} and the open ring form (MCTE) induced by UV irradiation. From the insert in Figure 1a, 5 min is needed to reach the saturated complexation, and observed rate constant can be estimated $4.0 \times 10^{-3}\,S^{-1}$.[3] In the reference experiment lacking of metal ions, we did not find the transformation from SNOTE to MCTE due to the fast conversion between the two forms. Our results indicate that the open ring form (MCTE) can be stabilized on the monolayer by introducing the metal ions. Moreover, for the SAMs of SNOTE immersed into Zn^{2+} solution but without UV irradiation, there is no absorbance around 480 nm in UV–vis spectra, suggesting that such absorbance must result from the complexation of the UV induced open ring form with metal ions. We have used X-ray photoelectron spectroscopy (XPS) to provide further information on the role of UV light in Zn^{2+} complexation with MCTE. The

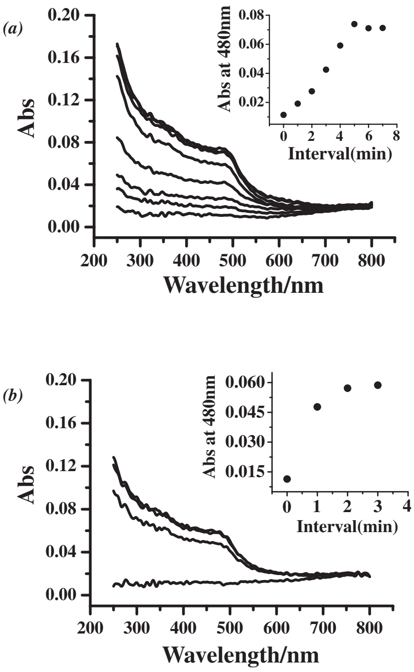


Figure 1. UV–vis reflection spectra of self-assembled monolayer of pure SNOTE (a) and co-assembled monolayer of SNOTE/SC_{12} (1:1 molar ratio in solution) (b) when complexing with Zn^{2+} controlled by ultraviolet irradiation. The irradiation interval is 1 min in 0.1 M Zn^{2+} aqueous solution. The inserts show the absorbance at around 480 nm increases with the immersing time under UV irradiation.

monolayer immersed in Zn^{2+} solution with UV irradiation shows a peak around 1021 eV in XPS, corresponding to Zn(II). Otherwise, without UV irradiation, there was no such obvious characteristic peak, though the monolayer was immersed in Zn^{2+} solution for 24 h.

The long saturation time for the pure SNOTE monolayer in complexation with zinc ions could be due to the densely packed spironaphthoxazine groups at surface. In order to confirm our assumption, we have fabricated a SNOTE and dodecanethiol co-assembled monolayer (SNOTE/SC_{12} = 1:1 molar ratio in solution) and studied the complexation process in a similar way. As shown in Figure 1b, it takes 2 min to reach the saturated complexation in this case. The observed rate constant is estimated as $2.7 \times 10^{-2}\,S^{-1}$, one level higher in magnitude than that of pure SNOTE monolayer. This result indicates that the introduction of the dodecanethiol as thinner-molecules results in the separation of SNOTE molecules from each other, which is responsible for the rapid complexation between the zinc ion and SNOTE under UV irradiation. The saturated absorbance in Figure 1a is higher than that in Figure 1b. This is understandable because of less spironaphthoxazine groups existing in co-assembled monolayer than in pure monolayer.

With more and more thinner-molecules of SC_{12} used, we further demonstrate that we are able to even isolate single SNOTE molecule at interface. For example, we prepared a co-assembled monolayer of SNOTE/SC_{12} (5:95 molar ratio in solution) on gold substrate. STM observation reveals that there are many well separated bright dots of about 0.4 nm in height, and the size feature of these dots is in agreement with single molecule, see Figure 2a. The larger holes are typical vacancies that usually exist in SAMs. Similarly, we used UV–vis spectroscopy to check whether there exist definitely a kinetic advantage for the isolated sensing species in SAMs. As shown in Figure 2b, the unique adsorption appears also at around 480 nm, contributed by the ion complexation under UV irradiation, though the saturated absorbance is much lower compared with the above two cases. As far as the kinetic process is concerned, the observed rate constant is $2.0 \times 10^{-2}\,S^{-1}$.

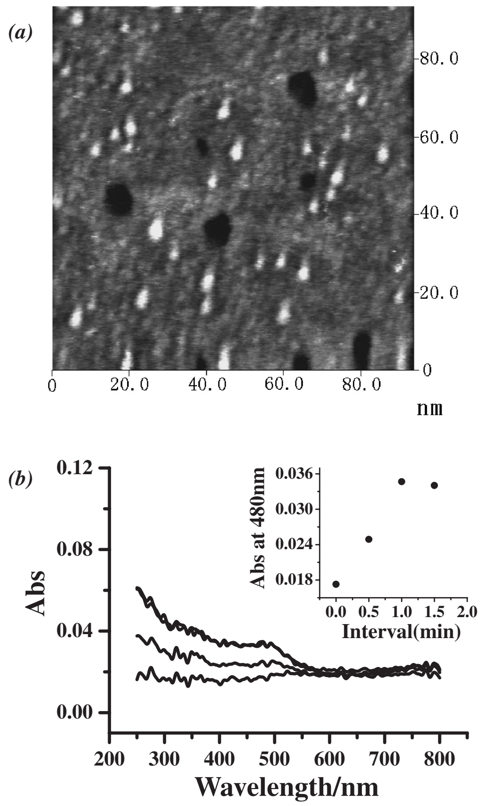


Figure 2. (a) STM image of co-assembled monolayer of SNOTE/SC_{12} (5:95 molar ratio in solution) on Au(111) surface. The light dots are well-separated SNOTE by thinner-molecules of dodecanethiol. (b) UV–vis reflection spectra of the above co-assembled monolayer complexing with Zn^{2+} controlled by ultraviolet irradiation. The irradiation interval is 30 s in 0.1 M Zn^{2+} aqueous solution.

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References and Notes

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7 ^{1}HNMR($CDCl_3$ TMS): $\delta = 7.860$–7.855 (d, 1H, $J = 2.5$ Hz), 7.732 (s, 1H), 7.633–7.615 (d, 1H, $J = 9$ Hz), 7.579–7.561 (d, 1H, $J = 9$ Hz), 7.217–7.202 (m, 1H, $J = 7.5$ Hz), 7.204–7.202 (d, 1H, $J = 1$ Hz), 7.093–7.078 (d, 1H, $J = 7.5$ Hz), 7.047–7.030 (m, 1H, $J = 8.5$ Hz), 6.897–6.882 (t, 1H, $J = 7.5$ Hz), 6.845–6.827 (d, 1H, $J = 9$ Hz), 6.584–6.568 (d, 1H, $J = 8$ Hz), 4.176–4.163 (t, 2H, $J = 6.5$ Hz), 2.770-2.761 (d, 3H, $J = 4.5$ Hz), 2.500–2.485 (t, 4H, $J = 7.5$ Hz), 1.883-1.869 (m, 2H, $J = 7$ Hz), 1.602–1.588 (m, 4H, $J = 7$ Hz), 1.525-1.510 (m, 2H, $J = 7.5$ Hz), 0.877–0.863 (t, 3H, $J = 7$ Hz). Elemental Analysis: Calcd C; 76.97, H; 9.31, N; 4.17%, found C; 76.63, H; 9.51, N; 4.29%.

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