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Tetrahedron Letters
Tetrahedron Letters 46 (2005) 349–351

Monitoring surface reactions optically in a self-assembled monolayer with a photochromic core

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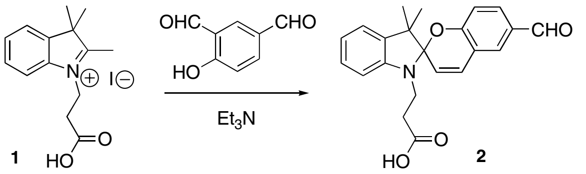
Received 2 September 2004; accepted 30 September 2004
Available online 30 November 2004

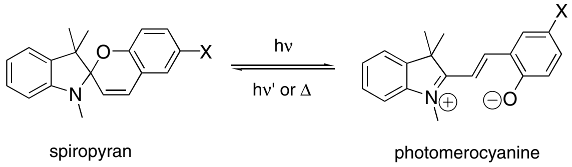
Abstract—Photochromic aldehyde-substituted spiropyran molecules were incorporated in a self-assembled monolayer structure and the rate of imine formation was determined by the shift in absorbance for the photomerocyanine upon UV irradiation.

Self-assembled monolayers (SAMs) are formed by the chemiabsorption of a molecule of interest onto a suitable surface. The two most common types of SAMs are the coverage of thiol containing molecules on coinage metals or the trialkoxy (or trihalo) silane molecules on glass.[1] SAMs have received tremendous interest due to their ability to control the wettability,[2] corrosion properties,[3] and the biocompatibility of the substrate.[4] Recently reactions at the 2D interface of the SAM have also received interest due to the ability to further tailor the substrate and to attach biomolecules to the surface.[5]

In the past we have attached photochromic chromophores onto glass surfaces through SAMs.[6] Photochromic molecules can be switched between two forms upon the application of an external light source.[7] Using photochromic spiropyrans the photogenerated merocyanine form can revert to the ground state spiropyran form either by the application of a visible light source or thermally. In the SAM structure the photochromic core allows the optical detection of monolayer coverage and monolayer properties through both the $\lambda_{\max}$ of the photogenerated merocyanine and the thermal lifetime of the merocyanine state. Additionally both of these optical signals can detect interactions at the solid/liquid interface of the SAM surface.



Scheme 1. Synthesis of aldehyde-substituted spiropyran for SAM attachment.



Previously the reaction between a surface exposed aldehyde and an amine to form an imine was studied at a SAM interface through grazing angle FTIR.[8] In the present study we optically detect the imine formation at the monolayer interface through a photochromic core. An aldehyde-substituted photochromic compound was prepared by reacting 1-(β-carboxyethyl)-2,3,3-trimethylindolenine iodide **1**[9] with commercially available 5-formylsalicylaldehyde to prepare **2** in a common reaction sequence for spiropyrans (Scheme 1).[10] Compound **2** was then attached to a SAM through standard procedures to generate a monolayer surface that has an aldehyde-substituted spiropyran exposed at the interface.[11] Upon exposure to 334 nm light the photomerocyanine with an aldehyde substituent was formed as evidenced by the peak growth at 574 nm. The half-life of this merocyanine to spiropyran interconversion in the SAM structure was found to be 173 ± 7 s with a toluene solution interface by monitoring the disappearance of

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Keywords: Self-assembled monolayer; Photochromic; Spiropyrans; Interfacial reactions.

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doi:10.1016/j.tetlet.2004.09.191

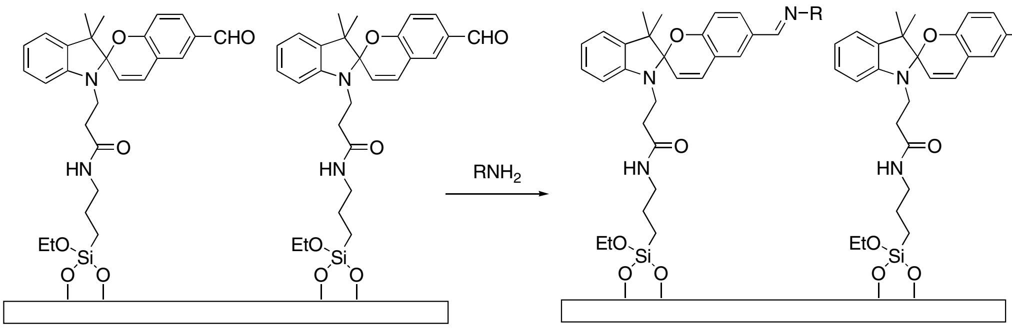

Figure 1. Formation of imine-substituted spiropyran at SAM interface.

the peak over time after the UV light source was turned off. The λ_{max} of this aldehyde-substituted photomerocyanine was shifted to a higher wavelength relative to the nitro-substituted photomerocyanine reported earlier due to the less electron-withdrawing substituent.

The aldehyde–spiropyran containing slides were reacted with excess propyl amine in a toluene solution at 50 °C.[12] As shown in Figure 1 these reaction conditions allow the formation of an imine-substituted spiropyran at the SAM interface. Periodically slides were removed from the constant temperature bath and were washed with toluene and acetone to remove any amine physisorbed to the surface.[13] The slides were then immersed in a pure toluene solution and irradiated with 334 nm light in order to generate the photomerocyanine form and the gradual appearance of a new peak at 592 nm was observed as seen in Figure 2. The λ_{max} of a photomerocyanine is highly sensitive to the nature of substituents. By converting an aldehyde-substituted spiropyran into an imine-substituted spiropyran the reaction change can be monitored by the λ_{max} shift in the photogenerated photomerocyanine. The imine-substituted photomerocyanine is thus shifted 18 nm relative to the aldehyde-substituted photomerocyanine (592 vs 574 nm). The ratio of the two peaks for a given reaction time was determined by fitting the area for the respective peaks from each absorption spectrum. The relative concentration of unreacted aldehyde spiropyran could then be determined as a function of time. The ln [aldehyde spiropyran] was plotted versus time to obtain a pseudo first order rate constant of 0.000564 M/s for the interconversion of the aldehyde to an imine at the monolayer interface as seen in Figure 3.

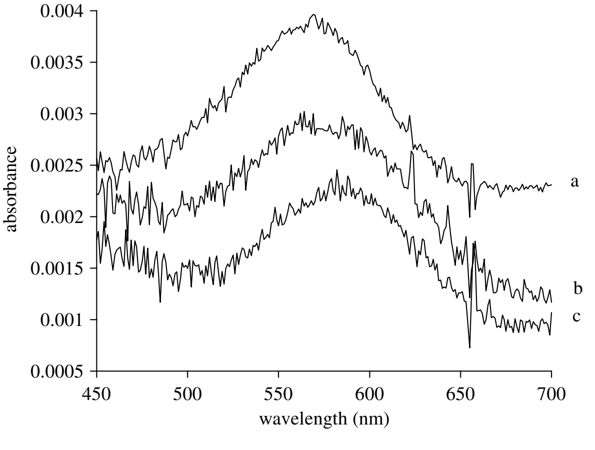

Figure 2. Optical absorbance of photomerocyanine. All spectra are obtained upon irradiating SAM with a mercury arc lamp with a 334 nm line filter. (a) Initial aldehyde-substituted spiropyran SAM, (b) after 30 min reaction with amine solution, (c) after 60 min reaction with amine solution.

In addition to the shift in λ_{max} between the aldehyde and imine-substituted photomerocyanine forms, the decay kinetics for the two photochromic structures also indicated the reaction to a less electron-withdrawing substituent. The aldehyde-substituted photomerocyanine to spiropyran interconversion had a thermal halflife of 173 ± 7 s for the SAM structure in toluene while the less polar imine substituent had a faster decay rate of 63.0 ± 6 s for the photomerocyanine to spiropyran interconversion in the SAM structure with a toluene interface. The shorter lifetime of the imine-substituted spiropyran versus the aldehyde is consistent with the shifted absorbance maximum as observed with a less electron-withdrawing substituent with other spiropyrans.

In conclusion the rate of imine formation at the 2D SAM interface was determined by the optical monitoring of the absorbance shift for a photochromic molecule at the interface. This procedure can be extended to compare reactions at 2D interfaces versus solution for

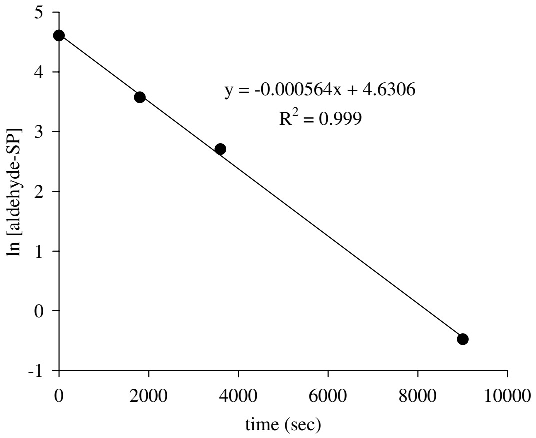

Figure 3. Kinetics of imine formation at SAM interface.

different solvents, temperatures, and reaction types. In addition it offers a procedure to monitor the attachment of biomolecules through the imine substituent at the photochromic core.

Acknowledgements

M.C.B. would like to acknowledge financial support from the Robert A. Welch foundation (AT-1388) for this project.

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11. To attach carboxylic acid derivatives to monolayer an amino functionalized surface was prepared by reacting a glass surface with 3-aminopropyltriethoxysilane (see Ref. 6 for procedure). The amine functionalized slides were immersed in a 5.2×10^{-5} M solution of **2** with an equimolar amount of 2-(H-Benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HBTU), and 10 equiv of diisopropylethylamine in DMF at room temperature. After 4 h the glass slides were removed and rinsed with methanol and acetone. The slides were then dried at room temperature.
12. The SAM prepared from **2** was immersed in a 1.61 M solution of propylamine in toluene and heated at 50 °C with a constant temperature bath. Slides were removed at time intervals and rinsed with toluene and acetone.
13. The washing was done immediately after removing the slides from the amine solution to prevent any physisorbed amine to react with an aldehyde at the surface before the optical properties of the slide could be tested.