Pergamon

Tetrahedron Letters 41 (2000) 3527–3530

TETRAHEDRON
LETTERS

Preparation of self-assembled monolayers with specific intermolecular interactions

Luis de Leon and Michael C. Biewer *

University of Texas at Dallas, Department of Chemistry, Box 830688, Richardson, TX 75083-0688, USA

Received 16 February 2000; accepted 15 March 2000

Abstract

A procedure is described to place different organic functionality spatially adjacent within a self-assembled monolayer formed between an alkyltriethoxysilane and a glass surface. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: molecular devices; spiro compounds; zwitterions; kinetics.

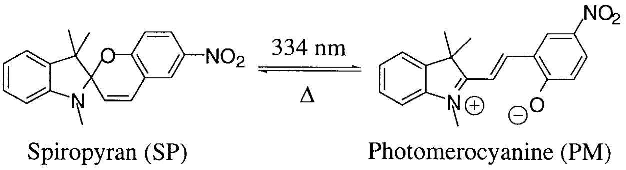
Self-assembled monolayers (SAMs) offer the ability to form an organized organic monolayer. By controlling the structure within this monolayer SAMs have potential for a wide variety of technological applications.[1] To further enhance the applicability of SAMs for device applications we have begun an investigation to study specific intermolecular interactions within the monolayer. Previously, SAMs have been prepared on a variety of surfaces including alkanethiols on gold and trialkoxysilanes on hydrophilic surfaces.[2] The goal of this project is to design a system where two different chemical entities can be placed adjacent within the SAM structure. By controlling the complimentarity of these two organic species the properties of the monolayer can be further enhanced.

Initial efforts of this SAM method have focused on the photochromic spiropyran to photomerocyanine interconversion. This system has been studied previously with the goal of creating an optical binary logic system.[3] The normally ground state spiropyran system can be photolyzed with ultraviolet light to generate the zwitterionic photomerocyanine. The absorbance changes during this interconversion from the ultraviolet range to the visible range (λ_{max} ~500–600 nm). If both of these states were thermally stable then an optical binary switch would be created with potential uses for logic gates. The photomerocyanine state is thermally unstable, however, and reverts back to the spiropyran. In order to prevent, or slow, this thermal reversion to the spiropyran state researchers have attempted two broad approaches: either to stabilize the PM state in fluid media through electrostatic interactions[4] or to incorporate the photochromic material in a rigid media which will hinder conformational mobility and hence slow the thermal reversion.[5]

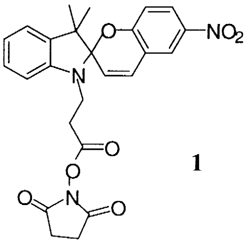
---

* Corresponding author.

PII: S0040-4039(00)00448-2



Spiropyrans have previously been included in a SAM structure.[6] Upon UV excitation the PM state is generated as evidenced by the appearance of an absorbance in the mid 500 nm range. To date only one study has determined the thermal kinetic decay of this PM back to the SP state in the SAM structure.[7] In our approach we prepared the SAM in a similar manner as Willner and Blonder,[6] by first etching the glass surface with an aqueous hydroxide solution, washing with deionized water, and drying the surface at 90°C overnight. After drying, the surface was treated with 3% 3-aminopropyltriethoxysilane in toluene at 95–105°C for 12 h. The slide was removed from the silanization solution and dried at 90°C for 24 h. Compound **1** was prepared as previously reported[6a] and the derivitized slide was heated at 50°C for 12 h in a 3×10^{-3} M solution of **1** in toluene to attach the spiropyran through an amide bond to the surface. The slide was then washed with toluene, methanol, and acetone to ensure removal of any unattached **1** molecules absorbed to the surface, and allowed to air dry for 1 h.



1

The slide containing the SAM of **1** was then photolyzed by directing a liquid light pipe from a 500 W Oriel Hg arc lamp containing a 334 nm mercury line filter. Upon UV excitation of one slide an absorbance is noted at 550 nm (see Fig. 1). In the dark this new peak decays with a rate constant of $6.28\pm0.16\times10^{-4}$ 1/s. This represents a lengthening of the half-life by a factor of 138 versus **1** in 10^{-6} M toluene solution (rate constant of $8.67\pm0.34\times10^{-2}$ 1/s). Presumably, this stabilization of the PM form is due to a constricted motion of the SP in the monolayer structure versus solution.

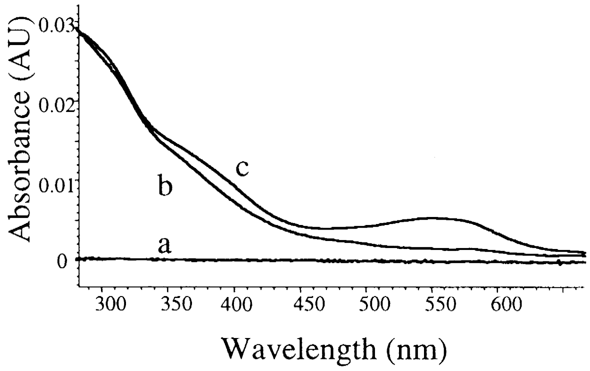
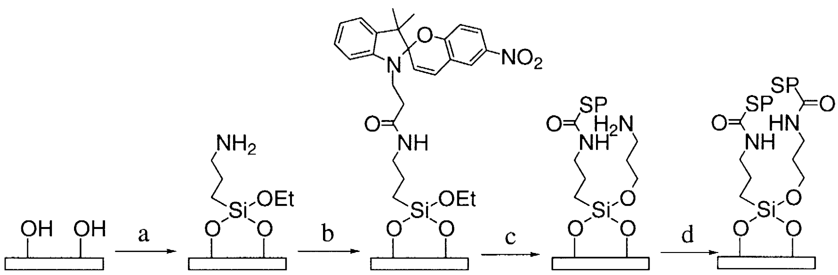


Fig. 1. Absorbance of PM in SAM structure: (a) slide after treatment with 3-aminopropyltriethoxysilane layer; (b) slide after covalently attaching the SP **1**; (c) slide after photolyzing with 334 nm light to generate PM with absorbance at 550 nm

In order to design specific intermolecular interactions a modification was performed on the SAM. As demonstrated by Vrancken et al. the predominant form of the silicon atom used to form the SAM is a bidentate bonding (see Scheme 1).[8] In this form two of the ethoxy groups of the starting material have formed ether bonds with the hydrophilic glass surface while the third ethoxy group is unreacted. Yin et al. have shown with glass beads that this third ethoxy group can be transesterified in a subsequent reaction with excess alcohol.[9] We wanted to determine if the SAM formed with an attached spiropyran could be modified to place a second organic group spatially adjacent to the spiropyran. If the spiropyran attached monolayer is in a tight van der Waals packing orientation presumably the silicon atom near the glass surface would not be sterically accessible for this transesterification. In order to test the possibility of this transesterification a SAM containing **1** was prepared. The slide was then cut in half and one half was kept as a reference while the second half was reacted with an excess of 3-propanolamine (3% in acetonitrile at 50°C for 12 h). After removing the slide from the 3-propanolamine solution it was rinsed with methanol and acetone, wiped dry, and allowed to dry at room temperature for 12 h. If a transesterification occurred a new primary amine group would be present. The slide was then further reacted by heating at 50°C for 12 h in a 3×10^{-3} M solution of **1** in toluene. The slide was then washed with toluene, methanol, and acetone. After drying at ambient conditions the slide was photolyzed as described previously. As seen in Fig. 2 the slide modified by attaching a second photochromic molecule has approximately twice the absorbance in the 550 nm peak compared to the slide prepared in the normal fashion.



a) 3-aminopropyltriethoxysilane, b) **1**, c) 3-propanolamine, d) excess **1**

Scheme 1. Preparation of modified SAM structure containing two spiropyran units

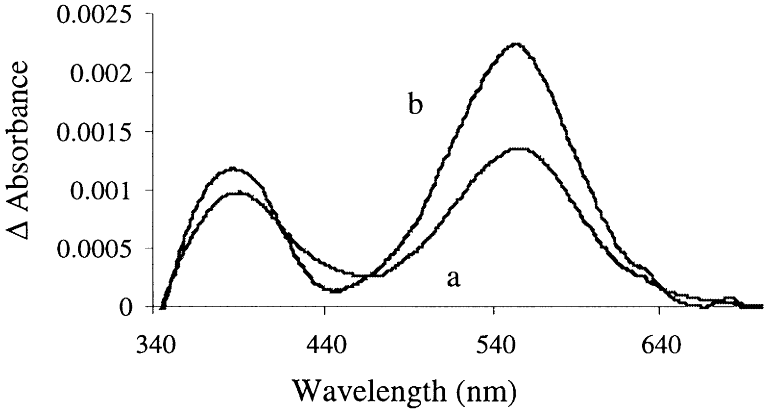


Fig. 2. Absorbance change for PM with modified SAM. Spectra were obtained by subtracting absorbance post-photolysis from pre-photolysis: (a) normal unmodified slide; (b) modified slide

A second indication that the two spiropyran molecules are spatially adjacent is the kinetic decay behavior for the photomerocyanine to spiropyran interconversion. In the initial procedure, where only one spiropyran is attached per alkyltriethoxysilane, the decay curve smoothly fits a first order decay. In the modified SAM procedure the decay curve does not fit a first order decay curve but rather is better described by a two-consecutive first order decay expression. This scenario indicates that a particular photomerocyanine is generated in two distinct electrostatic environments, as observed previously in other ordered environments.[5a] As seen in Table 1, two first order decays are observed, one which has a slower half-life than the single spiropyran and one which is faster. Therefore, there is a distinct difference between attaching only one spiropyran and using this modified SAM procedure which can attach a second organic molecule spatially adjacent to the spiropyran as evidenced by the increased absorption intensity and the change in decay profile. Potentially, any organic functionality can be placed adjacent to the initially prepared SAM containing the spiropyran moiety.

Table 1
Half-lifes for spiropyran **1** in different medium

medium	$t_{1/2}$ (s)	$t_{1/2}(2)$ (s)
toluene	8.0 ± 0.3	
SAM	1100 ± 30	
modified SAM	2960 ± 40	241 ± 21

* the $t_{1/2}(2)$ half-life refers to the second first order decay observed in the modified SAM

In summary, we have shown a new method to prepare SAMs on glass surfaces which allow two distinct organic species to be placed adjacent in the monolayer. We have used this SAM preparation procedure to stabilize the photogenerated photomerocyanine intermediate. We are currently preparing potential organic stabilizers for the photomerocyanine to attach in this method to increase the lifetime of the photogenerated state by specific intermolecular interactions which will be reported in due course.

Acknowledgements

This work was supported by the Robert A. Welch Foundation (AT-1388) and the University of Texas at Dallas.

References

1. see: Clegg, R. J.; Reed, S. M.; Hutchinson, J. E. *J. Am. Chem. Soc.* **1998**, *120*, 2486–2487.
2. see: Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 550–575.
3. Feringa, B. L.; Jager, W. F.; de Lange, R. *Tetrahedron Lett.* **1993**, *49*, 8267–8310.
4. (a) Suzuki, T.; Lin, F.; Priyadashy, J.; Weber, S. G. *Chem. Commun.* **1998**, *24*, 2685–2486. (b) Inouye, M.; Akamatsu, K.; Nakazumi, H. *J. Am. Chem. Soc.* **1997**, *119*, 9160–9165.
5. (a) Allcock, H. R.; Kim, C. *Macromolecules* **1991**, *24*, 2846–2851. (b) Cabrera, I.; Kongauz, V.; Ringsdorf, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1178–1180. (c) Tomioka, H.; Itoh, T. *Chem. Commun.* **1991**, *8*, 532–533.
6. (a) Willner, I.; Blonder, R. *Thin Solid Films* **1995**, *266*, 254–257. (b) Willner, I. *Acc. Chem. Res.* **1997**, *30*, 347–356.
7. Galvin, J. M.; Schuster, G. B. *Supramolecular Science* **1998**, *5*, 89–100.
8. Vrancken, K. C.; van der Voort, P.; Gillis-D'Hamers, I.; Vansant, E. F. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 3197–3200.
9. (a) Nemeth, S.; Yin, R.; Ottenbrite, R. M.; Siddiqui, J. R. *Polym. Prepr.* **1997**, 38(2), 365–366. (b) Yin, R.; Ottenbrite, R. M.; Siddiqui, J. R. *Polym. Prepr.* **1996**, *37*, 751–752. (c) Yin, R.; Ottenbrite, R. M.; Siddiqui, J. R. *Polym. Prepr.* **1995**, *36*, 449–450.