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Studying monolayer/solvent interactions with a photochromic compound in a self-assembled monolayer

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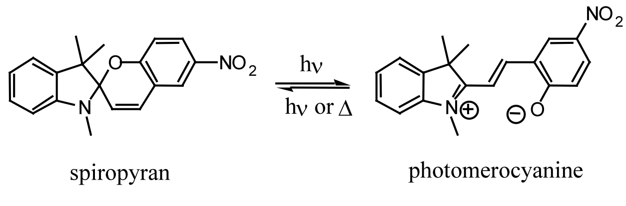
Abstract—Photochromic materials were incorporated within a structured self-assembled monolayer and the decay rate of the photomerocyanine was determined with different monolayer–solute interactions. © 2002 Elsevier Science Ltd. All rights reserved.

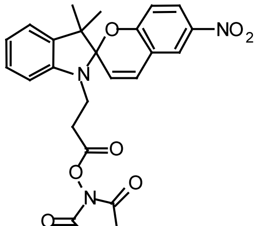
Self-assembled monolayers (SAMs) offer the ability to control the characteristics of a surface. By controlling the surface properties SAMs have been studied for interfacial friction control, sensing capabilities and as models for membranes.[1] The two most common SAM systems studied are sulfur on coinage metals or trialkoxy (or trihalo) silanes on hydrophilic surfaces.[2] The formation of SAMs with trialkoxysilanes on glass surfaces offers a more robust surface due to the covalent bonds formed at the surface, thereby eliminating the potential migration of organic groups within the monolayer observed in the sulfur on gold system.[3] Either system, however, offers a quick and convenient method to prepare monolayers with a diverse range of organic functionality.



Photochromic compounds are converted between two or more forms upon absorption of an appropriate wavelength of light. One of the most studied photochromic systems is the spiropyran to photomerocyanine interconversion.[4] Upon application of ultraviolet light the spiropyran is converted to the colored photomerocyanine form which in the dark anneals back to the spiropyran.

These two forms have different electronic properties and hence can be used as a molecular switch. Previously spiropyrans have been included in monolayers both with sulfur on gold and with trialkoxysilane SAMs. Once included in the monolayer the switching mechanism was used to control the function of biomaterials[5] and also as a potential means to control liquid crystal alignment on the monolayer.[6]

Previously both we[7] and others[6] have reported the decay rate of the photomerocyanine generated from **1** in the dark when included in a SAM with an air interface. In order to potentially build devices using photochromic materials in a SAM the focus of this study was to determine the decay rate of the photo-



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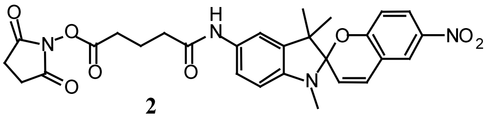

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Keywords: spiropyrans; photochromic compounds; self-assembled monolayer.

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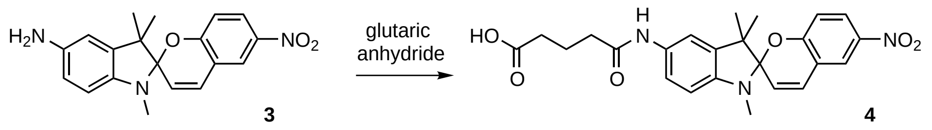

Scheme 1. Synthesis of spiropyrans with different appendage sites.

chromic material in the SAM with various liquid interfaces and to test the effect of the orientation of the photochromic material relative to the surface. Previously compound **1** had been attached within the SAM by first reacting the hydrophilic glass surface with triethoxysilyl propyl amine to generate an amine terminated surface which was subsequently reacted with the activated ester **1** to covalently link the spiropyran through an amide bond.[6,7] The point of attachment, and hence orientation of the photochromic material to the surface, could be altered by reacting the previously reported amine substituted spiropyran **3**[8] with glutaric anhydride to synthesize **4** (Scheme 1). The acid was then converted to the succinyl ester by a DCC coupling procedure to create **2**. Using similar procedures as the formation of SAM with **1**, a SAM was then formed with **2** on glass surfaces differing in the functionality exposed on the surface compared to **1**.

After SAM formation the slides were place in a cuvet containing various solvents. Upon irradiation with 334 nm light[9] the photomerocyanine was generated as evidenced by the appearance of an optical absorption as seen in Fig. 1 between 500 and 600 nm depending upon the polarity of the solvent. The surface coverage for compounds **1** and **2** were determined to be 180 and 65 Å^2/molecule,[10] respectively, compared to the calculated cross sectional areas of 97 and 56 Å^2 for **1** and **2** assuming the molecules are oriented perpendicular to the glass surface. These values are consistent to other similarly sized chromophores attached to glass slides.[11] After the maximum absorption of the photochromic peak was obtained the decay of this peak was monitored in the dark over a period of hours. The decay was fitted with a first order exponential to obtain the half-life of the photomerocyanine in different solvents as listed in Table 1 for compounds **1** and **2**.

As can be seen from Fig. 2, the decay rate of the photomerocyanine was related to the empirical solvent constant [$E_T(30)$] thus indicating the affect of the solvent polarity on the monolayer–solute interactions. Compound **2** decayed at a slower rate in all solvents due to the added stabilization of the photomerocyanine with the electron donating amide nitrogen appendage *para* to the charged indolenine nitrogen in the ring.

Another trend is that both compounds **1** and **2** are less sensitive to the solvent characteristics in the SAM structure compared to solution. This is indicated first in the change in λ_{max} with the different solvents. In the monolayer structure the λ_{max} does not change with solvent polarity as pronounced as in solution (comparing methanol to toluene for **1**: $\Delta\lambda_{max}$ (solution) 62 nm, $\Delta\lambda_{max}$ (SAM) 24 nm). The monolayer structure thus 'insulates' the photomerocyanine from the solvent molecules to some extent. The decay rates in the monolayer are also less sensitive to the change in solvent polarity than in solution. As seen in Fig. 3, the slope of the linear free energy relationship for log k versus empirical solvent constant is greater for the solution studies compared to the monolayer structure for compound **1**. Both effects indicate a stability offered by the monolayer structure.

In conclusion the decay rates of photochromic compounds incorporated within a SAM structure were determined for the first time when in contact with

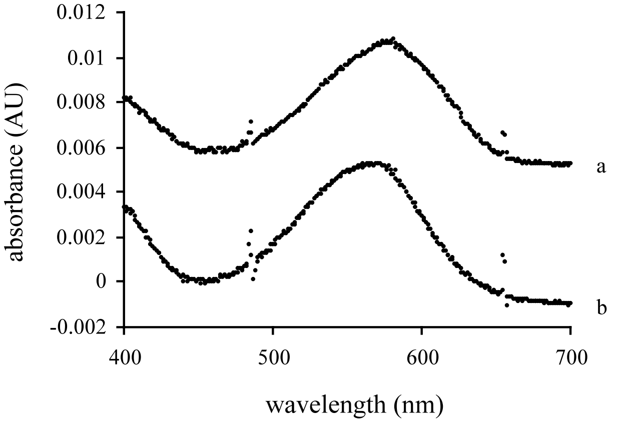

Figure 1. UV–vis of photogenerated photomerocyanine in SAM structure. (a) Slide of **2** in SAM with toluene. Both spectra are difference between slide before and after photolysis with 334 nm light. (b) Slide of **1** in SAM with toluene.

Table 1. Decay characteristics of photomerocyanines studied

System	Solvent	λ_{max}	$t_{1/2}$ (min)[a]
1	Methanol	543	10.45±0.08
1	Acetonitrile	570	0.758±0.073
1	Toluene	605	0.0618±0.0003
1	Acetone	575	0.327±0.010
1	Ethyl acetate	585	0.180±0.005
2	Toluene	611	0.102±0.006
1/SAM	Water	541	30±9
1/SAM	Methanol	547	24±6
1/SAM	Acetonitrile	550	19±3
1/SAM	Toluene	571	13±1
2/SAM	Water	544	50±20
2/SAM	Methanol	548	42±17
2/SAM	Acetonitrile	565	33±17
2/SAM	Toluene	578	20±2

[a] Listed error is from fit of first order decay to absorbance versus time curve for photomerocyanine in the dark

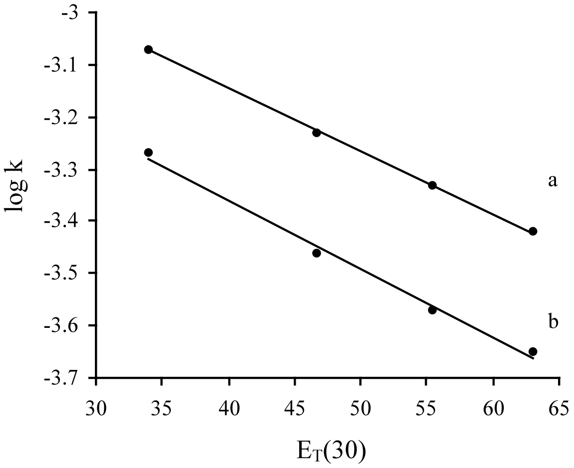

Figure 2. Relationship of photomerocyanine decay rate in SAM versus solvent. (a) SAM with **1**. (b) SAM with **2**.

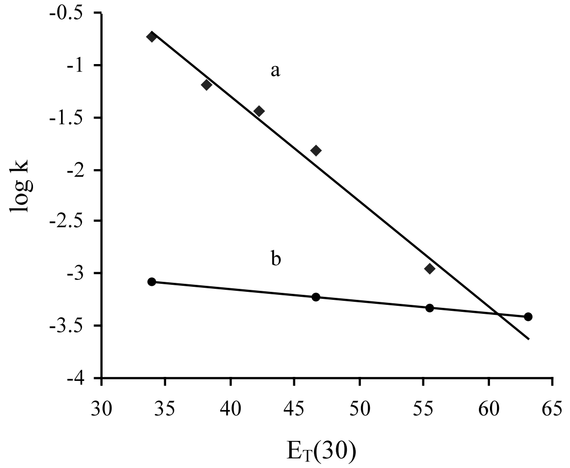

Figure 3. Effect of solvent upon photomerocyanine decay in different medium. (a) **1** in solution only. (b) **1** in SAM.

various solvents. The monolayer–solute interaction is related to the polarity of the solvent used. Potentially this system will allow the use of an optical signal to record interactions between analytes in solution and the structured monolayer.

Acknowledgements

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