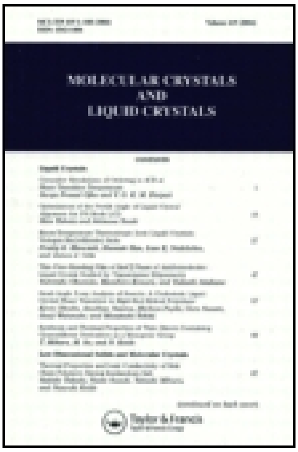


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Solvent Effect on Photochromic UV-Sensing of a Self-Assembled Spiroxazine Monolayer

Sungwook Choi [a], Sungho Jin [b], Yeongsoon Gal [c], Jaeho Kim [d], Sunghoon Kim [e] & Kwangnak Koh [f]

[a] Graduate School of Sensor Eng., Kyungpook National University, Taegu, 702-701, Korea

[b] Dept. of Chemistry Education, Pusan National University, Pusan, 609-735, Korea

[c] Chemistry Division, Kyungil University, Kyungsangbuk-do, 712-701, Korea

[d] Dept. of Molecular Science and Technology, Ajou University, Suwon, 442-749, Korea

[e] Dept. of Dyeing and Finishing, Kyungpook National University, Taegu, 702-701, Korea

[f] Dept. of Chemical Eng., Kyungpook National University, Taegu, 702-701, Korea

Version of record first published: 29 Oct 2010

To cite this article: Sungwook Choi, Sungho Jin, Yeongsoon Gal, Jaeho Kim, Sunghoon Kim & Kwangnak Koh (2002): Solvent Effect on Photochromic UV-Sensing of a Self-Assembled Spiroxazine Monolayer, Molecular Crystals and Liquid Crystals, 377:1, 229-232

To link to this article: http://dx.doi.org/10.1080/713738487

Mol. Cryst. Liq. Cryst., Vol. 377, pp. 229-232
Copyright © 2002 Taylor & Francis
1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290088960

Solvent Effect on Photochromic UV-Sensing of a Self-Assembled Spiroxazine Monolayer

SUNGWOOK CHOI[a], SUNGHO JIN[b], YEONGSOON GAL[c],
JAEHO KIM[a], SUNGHOON KIM[d] and KWANGNAK KOH[f]

[a]*Graduate School of Sensor Eng., Kyungpook National University,*
Taegu 702-701, Korea,
[b]*Dept. of Chemistry Education, Pusan National University,*
Pusan 609-735, Korea,
[c]*Chemistry Division, Kyungil University, Kyungsangbuk-do 712-701, Korea,*
[d]*Dept. of Molecular Science and Technology, Ajou University,*
Suwon 442-749, Korea,
[e]*Dept. of Dyeing and Finishing, Kyungpook National University,*
Taegu 702-701, Korea and
[f]*Dept. of Chemical Eng., Kyungpook National University,*
Taegu 702-701, Korea

Abstract
The photochromic behavior of spiroxazine by UV irradiation can be affected by some solvents surrounding the photochromic dye. To investigate this solvent effect, we formed a self-assembled monolayer of a synthesized spiroxazine derivative on a gold surface. The solvent effect on photochromic behavior was studied by using surface plasmon resonance (SPR). The subtle photochromic behavior of the monolayer in different solvents under UV irradiation can be measured efficiently through comparison of their SPR angle shifts.

Keywords photochromism; spiroxazine; self assembled monolayer

INTRODUCTION

A system is said to be photochromic when it comprises a reversible photochemical reaction of a single chemical species. Photochromic materials have been the subject of intense recent investigation because of their wide variety of potential applications including sunlightactivated, self-colored glasses and optical memory media.[1] Among these materials, spiropyran and spiroxazine have been extensively studied due to their ability to improve resistance to prolonged UV irradiation, which confers greater commercial importance.

In recent years, interest in the properties of thin-film organic materials has grown enormously with regards to Langmuir-Blodgett (LB) film and self-assembled monolayer (SAM). SAM is a well-packed quasi-crystalline monolayer which offers multiple advantages as substrates for the study of organic surface chemistry. SAM on metal surfaces has received considerable attention because of the importance of establishing how surface properties can be altered by light and how the behavior of SAM is affected by structural rigidity.[2]

Since the SPR technique has very high sensitivity, it is a good tool to measure precise characteristics of a photochromic ultra thin-film. Therefore, we tried to monitor single molecular behavior in spiroxazine SAM according to variation of only one carbon-different solvents (pentane, hexane, and heptane) with SPR technique.

EXPERIMENTAL

Spiroxazine derivative (**1**) and its monolayer were prepared according to a previously reported method (Figure 1).[2] A gold-deposited glass slide was immersed in a 1.0×10^{-2} M cystamine hydrochloride aqueous solution for 2 hours and then rinsed with deionized water. After rinsing, the cystamine adsorbed gold layer was treated with a 1.0×10^{-2} M ethanolic solution of 1-ethyl-3-(3-(dimethylamino)propyl)-carbodiimide (EDC) and 5.0×10^{-4} M of spiroxazine dye derivative (**1**) for 2 hours. The resulting monolayer was rinsed several times with deionized water and dried.

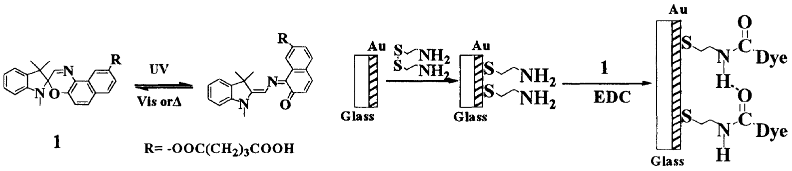


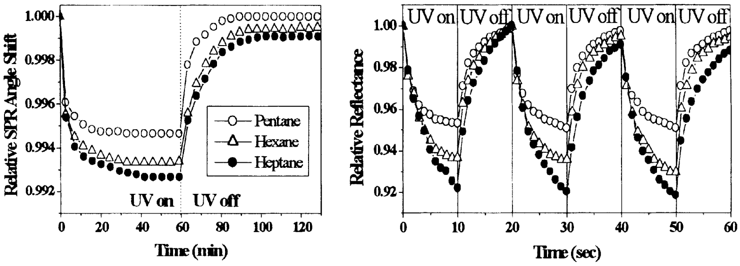
Figure 1 Stepwise organization of the spiroxazine monolayer on Au layer.

The SPR measurements were performed with a homemade

Kretschmann configuration apparatus descrived in a published report.[2] In order to observe the photochromic properties of the monolayer containing spiroxazine dye (**1**), we measured the SPR angle shifts of the SAM in each solvent, such as pentane, hexane, and heptane. Additionally we investigated the variation of intensity of reflected light in UV-on and UV-off state with an interval of 10 seconds at a fixed SPR incident angle of 60.38° in pentane, 63.57° in hexane, and 64.28° in heptane to examine the time profile of the photoisomerization process in each solvent.

RESULTS AND DISCUSSION

The Fourier transform infrared reflection absorption spectroscopy (FT-IR RAS) showed that the bands of 1653, 1740, 3163 cm^{-1} are assigned as -C=O stretching mode of amide, -C=O stretching mode of ester, and –N-H stretching mode of amide, respectively. These results indicated that spiroxaizne monolayer performed at the cystamine monolayer of the Au substrate.



(a) (b)

FIGURE 2 (a) SPR resonance angle shifts before and after UV irradiation until fully saturation. (b) The intensity variation of reflected light in UV- on and off state with interval of 10 seconds.

Figure 2(a) shows the SPR curves for the SAM with the photochromic spiroxazine dye (**1**) before and after exposure to UV irradiation in different solvents. Under UV irradiation, the spiro form of the monolayer turns to a merocyanine form and the SPR angle shifts to a negative region. This phenomenon can be explained by the formation of the photoinduced opened-spiroxazine form i.e., photochromism. Additionally, to compare the subtle different degree of photochromism in each solvent, the reflectance was measured at a fixed SPR incident angle (Figure 2(b)). The change of the reflectance diminished when decreasing the number of the carbons in the solvent used.

TABLE 1 Polarity ($E_T(30)$), viscosity (η), and relative SPR angle shift ($\Delta\theta$) after UV irradiation for 60 min.[4,5]

Solvent	$E_T(30)$ (Kcal mol^{-1})	η (mPa·s)	$\Delta\theta$
Pentane	31.0	0.24	0.00535
Hexane	31.0	0.31	0.00662
Heptane	31.1	0.42	0.00736

Factors that can influence the rate of photoisomerization are the polarity of the medium, the viscosity of the solvent, and hydrogen bonding.[3] As Table 1 indicates, the polarity of each solvent makes little difference. Moreover, the hydrogen bonds between each solvent and the dye also do not exist. Therefore, we can recognize that the rate of photoisomerization is primarily affected by the viscosity of each solvent and that such mechanical action of molecules may differ according to the viscosity of the solvent. Additionally, we can sufficiently monitor the subtle difference of photochromic behavior by SPR technique using the difference of only one carbon chain length of each solvent.

Acknowledgments

This work was supported by grant No. 2000-2030800-001-3 from the Basic Research Program of the Korea Science & Engineering Foundation.

References

[1] C. John and J. Robert, Organic photochromic and themochromic compounds I Ⅱ, Plenum Press, Now York (1999).
[2] S. Kim, S. Lee, J. Park, J. Kim and K. Koh, Dyes and Pigments, **45**, 51 (2000).
[3] M. Rappon and R. Syvtski, Jounal of Photochemistry and Photobiology A: Chemistry, **94**, 243 (1996).
[4] C. Reichardt, Chem. Rev., **94**, 2319 (1994)
[5] R. David and H. Frederikes, CRC Hand book of chemistry and physics, CRC Press., Inc., Tokyo (1994).