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Dyes and Pigments 45 (2000) 51–57

DYES and PIGMENTS

# The preparation and spectroscopic study of self-assembled monolayers of a UV-sensitive spiroxazine dye on gold

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Received 23 October 1999; received in revised form 3 December 1999; accepted 12 December 1999

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## Abstract

The molecular orientation and structure of self-assembled monolayers on gold of a spiroxazine dye have been investigated using visible absorption and infrared spectroscopy. The absorption spectra of the photochromic spiroxazine dye in various solvents exhibited positive solvatochromism, a finding which strongly suggests that the dye structure changes to an open chain form which may be a keto type structure. A spiroxazine dye monolayer was deposited on a gold surface using a stepwise method that involved the covalent linkage of the dye to a cystamine monolayer-modified gold. The molecular structure of the self-assembled monolayer of the spiroxazine dye was investigated using Fourier-transform reflection absorption spectra. © 2000 Published by Elsevier Science Ltd. All rights reserved.

*Keywords:* Self-assembled monolayer (SAM); Spiroxazine; Solvatochromism; Cystamine; Reflection absorption spectra

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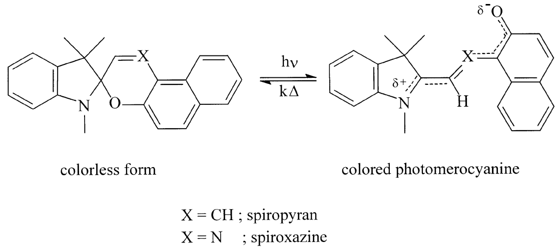
## 1. Introduction

A photochromic compound is characterized by its ability to undergo a reversible colour change. Although photochromic compounds have attracted significant attention because of their potential use as sunlight-activated, self-coloured glasses and optical memory media, they still await major commercial exploitation.

One of the prime reasons for the lack of industrial applications for photochromic materials, particularly organic photochromic compounds, is their poor durability. Although the photochromism of spiropyran has been extensively studied [1,2], only little work has been carried out on spironaphthoxazine dyes. These two classes of compounds are similar in many respects, but the replacement of the benzopyran ring by a naphthoxazine ring, which results in spironaphthoxazine, greatly improves resistance to prolonged UV irradiation, which confers greater commercial importance [3].



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PII: S0143-7208(00)00002-4

We have previously reported on the synthesis, spectral properties and solvatochromic properties of spironaphthoxazines [4–6].

Interest in the properties of thin film organic materials, especially with regards to organized mono- and multilayer structures prepared by Langmuir–Blodgett and self-assembly techniques, has grown enormously in recent years. Self-assembled monolayers (SAMs) are crystalline, chemisorbed organic monolayers that are formed on a solid substrate by the spontaneous organization of molecules [7,8]. Recent interest in SAM systems stems from a recognition of the potential for their use in detailed studies of structure–function relationships at solid–liquid interfaces.

The monolayers prepared from sulfur-containing species, such as thiols and disulfides, at gold surfaces have been especially well-studied because of their tendency to form quasi-crystalline monolayers with well-defined structures [8]. The self-assembly process of alkanethiols [$HS–(CH_2)_n–CH_3$] on gold is initiated by strong interactions between the sulfur head-group and the gold surface which are believed to result in chemisorption of the molecules as thiolates, which forces them to become commensurate with the gold lattice [9–11].

A crystalline film at room temperature can only be formed if the attractive, tail-to-tail interactions due to lateral van der Waals' forces are strong enough to align the tails in a parallel manner. The technological impetus for this rebirth, namely the relevance of such structures and materials to adhesion [12], lubrication [13], microelectronics [14], photochemical processes [15] and electrochemical [16] processes as well as biological interfaces [17], has been discussed extensively.

In previous studies, we have examined the preparation and structural characterization of a highlyordered, hydrogen-bonding, squarylium dye-containing alkanethiol monolayer by the use of visible absorption, IR spectroscopy, contact angle measurement and atomic force microscopy (AFM). To the best of our knowledge, there are, as yet, no published studies on the synthesis and characterization of spiroxazine dye-containing alkanethiols for SAMs. This paper concerns the preparation and properties of a photochromic, spiroxazine-containing alkanethiol monolayer on gold.

## 2. Experimental

### 2.1. Characterization of products

Melting points were determined using an Electrothermal IA 900 and are uncorrected. Elemental analyses were recorded on a Carlo Elba Model 1106 Analyzer. Mass spectra were recorded using a Shimadzu QP-1000 spectrometer with an electron energy of 70 eV and direct sample introduction. $H^1$ NMR spectra were recorded in $CDCl_3$ using a Varian Unity Inova 300 MHz FT-NMR spectrometer using TMS as internal standard. UV–visible spectra were recorded on a Shimadzu 2100 spectrophotometer.

### 2.2. Synthesis of spiroxazine dye and intermediate

#### 2.2.1. Intermediates **3**, **4** and **6**

2,3,3-Trimethylindolenine **1** (15.9 g, 0.1 mol) and bromoethanol **2** (13.7 g, 0.11 mol) were refluxed for 8 h in 100 $cm^3$ of chloroform. The solvent was removed in vacuo and then 20 $cm^3$ of ethyl acetate were added to the reaction mixture. The precipitated solid was filtered, washed with chloroform and dried, to give **3** as a red solid in 24% yield, mp 195–196°C. Compound **3** (6.3 g, 22.3 mmol) thus obtained was added to 300 $cm^3$ of 10% aqueous NaOH solution, which was then extracted using 200 $cm^3$ of chloroform. The extract was concentrated by rotary evaporation and the resulting oily product collected and used in the next step without further purification. Yield 3.45 g (76.2%); EA calcd: $C_{13}H_{17}NO$ (C, 76.84; H, 8.37; N, 6.89), found: (C, 76.79; H, 8.89; N, 6.25); $m/z$ ($M^+$): 203.

To a benzene solution (20 $cm^3$) of glutalic anhydride **5** (1.1 g, 10 mmol) and conc. hydrochloric acid (2 $cm^3$), **4** (2 g, 9.8 mmol) in benzene (5 $cm^3$) was added and the mixture stirred under reflux for 24 h. The solvent was evaporated under reduced pressure and washed with ethyl acetate to give **6** in 75.6% yield. $\nu$ $cm^{-1}$ (KBr): 1730, 1250; $m/z$ ($M^+$); 317.

#### 2.2.2. Spiroxazine dye **8**

A mixture of **6** (3.5 g, 11 mmol) and nitrosonaphthol **7** (1.9 g, 11.1 mmol) in acetone (20 $cm^3$) was stirred under reflux for 10 h. The solvent was distilled off under reduced pressure and the residual product purified using column chromotography with hexane: ethyl acetate (v/v, 10:3) as eluent to give **8**. Mp; 45–46°C, yield 0.6 g (12%) δH ($CDCl_3$) 8.6–8.5 (1H, d), 7.8–7.7 (1H, d), 7.8 (1H, s), 7.7–7.6 (1H, d), 7.6–7.5 (1H, t), 7.4–7.3 (1H, t), 7.2–7.1 (1H, t), 7.1–7.0 (1H, d), 7.0–6.9 (1H, d), 6.9–6.8 (1H, t), 6.7–6.6 (1H, d), 4.4–4.2 (2H, m), 3.6–3.4 (2H, m), 2.5–2.3 (2H, m), 2.0–1.8 (2H, quint), 1.3–1.2 (6H, s): EA calcd; $C_{28}H_{28}\,N_2O_5$ (C, 71.17; H, 5.97; N, 5.93), found; (C, 70.88; H, 6.42; N, 5.51); $m/z$ ($M^+$); 472.

### 2.2.3. *Preparation of self-assembled monolayer*

A gold surface was prepared by the electron-beam evaporation of 30 Å of nickel–chromium as an adhesion promoter, followed by 500 Å of gold, on to a glass slide. The stepwise chemical assembly of a spiroxazine monolayer was performed by the covalent linkage of the carbonyl unit of spiroxazine dye **8** to a cystamine-monolayer-modified gold surface. A gold deposited glass slide was immersed in a $1\times10^{-2}$ M cystamine hydrochloride aqueous solution for 2 h and then rinsed with deionized water. After rinsing, the cystamine adsorbed gold layer was treated with a $1\times10^{-2}$ M ethanolic solution of 1-ethyl-3-(3-(dimethylamino) propyl)-carbodiimide (EDC) and $5\times10^{-4}$ M of the spiroxazine dye **8** for 12 h. The resulting monolayer was rinsed several times with deionized water and dried in nitrogen gas [18].

### 2.2.4. *Infrared measurement*

Fourier transform infrared reflection absorption spectroscopy (FTIRRAS) was carried out using a Nicoler Magma-IRTM 500 spectrometer. A narrow band HgCdTe detector, cooled with liquid nitrogen, was used to detect the reflected light. For the FTIRRAS measurements, a Graseby Space grazing angle reflectance accessory equipped with a polarizer was used at 80° all spectra were collected with 2 $cm^{-1}$ resolution. To minimize the signal-to-noise ratio, several hundred scans were obtained. Cast films of the spiroxazine **8** were prepared from an ethanolic solution on a gold plate.

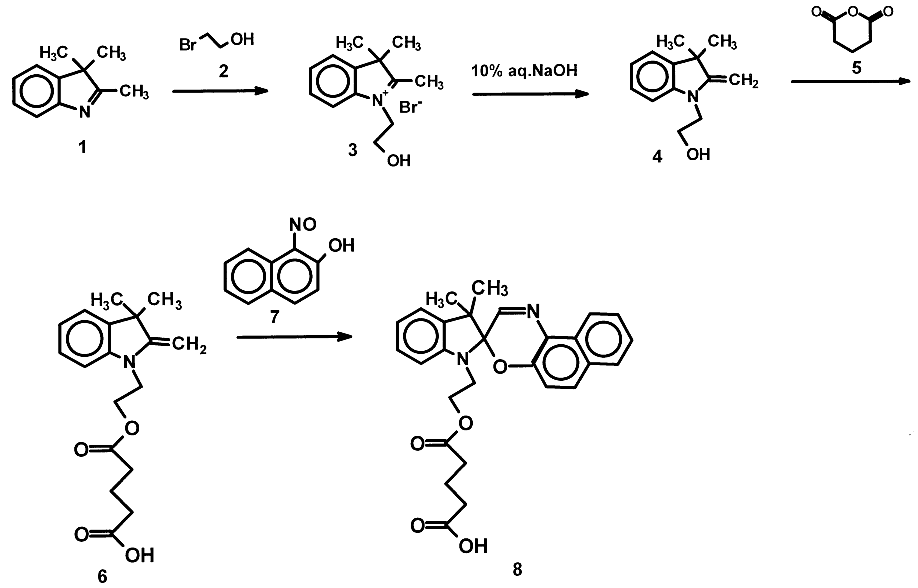
### 2.2.5. *Visible absorption spectra*

A multi-channel photodiode detector (MCPD) obtained from Otsuka Electronics, Co. was used to obtain visible reflection absorption spectrum (RAS) of the SAM on the gold surface. An $I_2$ light source was projected and collected by a Y-type optical fibre; the uv-vis solution spectra were measured using a JASCO V-55 spectrophotometer.

## 3. Results and discussion

In general, spiroxazine and structurally related organic photochromic compounds are synthesized using a thermal condensation reaction of the corresponding alkylidene heterocycle or its conjugate acid with ortho-hydroxy nitroso aromatic derivatives. They form readily in most polar organic solvents at or near the reflux temperature and can be purified using recrystallization or column chromatography. The synthetic route to the spiroxazine dye **8** is outlined in Scheme 1.

The reaction of Fisher's base derivative **6** with nitrosonaphthol **7** gave the spiroxazine dye **8** in 12% yield. As in the case of spiropyrans, a dilute solution of the spiroxazine dye in various solvents was colourless and became intensely blue upon irradiation with uv light or sunlight; the blue colour of the solution disappeared rapidly once the light source was removed. It was difficult to measure the absorption spectrum of the coloured compound at room temperature, since its thermal decay was rapid. Fortunately, the thermal decay of the coloured form proceeded slowly at low temperature. The absorption spectra of dye **8** in various solvents were measured in a dry ice–acetone bath. The open chain form of the spiroxazine dye such as the keto form (**8a**) or the resonance form (**8b**) or the zwitterionic form (**8c**) could exhibit either a bathochromic or a hypsochromic shift. If the dye molecules possess a permanent dipole, the polar solvent lowers the energy of the ground state more than the excited state and the solvent produces a hypsochromic shift (negative solvatochromism) [19]. In many coloured molecules, the ground state is less polar than the excited state and so a polar solvent will tend to stabilize the excited state more than the ground state, giving rise to a bathochromic shift (positive solvatochromism). Dimroth et al. have suggested that the transition energy for a pyridinum-*N*-phenoxide



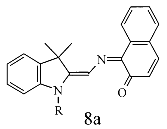
Scheme 1.

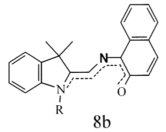
betain dye, expressed in kcal mol$^{-1}$, be used as a polarity parameter [19]; this parameter is referred to as the $E_T$ value. Uv–vis spectral data of the open form of dye **8** and the $E_T$ value of the solvents are given in Table 1.

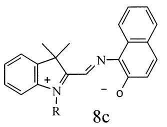
In this work, reasonably linear plots were obtained on plotting $\lambda_{max}$ versus the solvent parameter, $E_T$ (Fig. 1). As the solvent polarity increased, a bathochromic shift was observed (i.e. positive solvatochromism) which is indicative of the open chain form which absorbs near the $\lambda_{max}$ (600 nm) of the keto structure **8a**.

Table 1
$\lambda_{max}$ of the open form of the spiroxazine dye **8** in various solvents

| Solvent | $E_T$ (kcal mol$^{-1}$) | $\lambda_{max}$ (nm) |
|---|---|---|
| EtOH | 51.9 | 620 |
| Acetone | 42.2 | 600 |
| $CH_2Cl_2$ | 41.2 | 578 |
| $CHCl_3$ | 39.1 | 575 |
| THF | 37.4 | 570 |
| Toluene | 33.9 | 570 |
| $CCl_4$ | 32.4 | 560 |


8a


8b


8c

A cystamine monolayer was first assembled on a gold surface and the spiroxazine dye **8** was then coupled to the base monolayer using a small amount of EDC as recently described [20,21] (Scheme 2). Over the years, EDC has emerged as

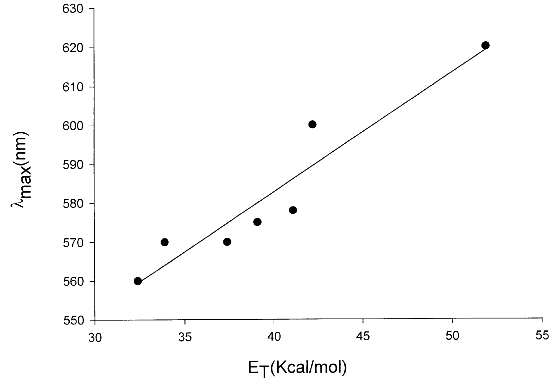
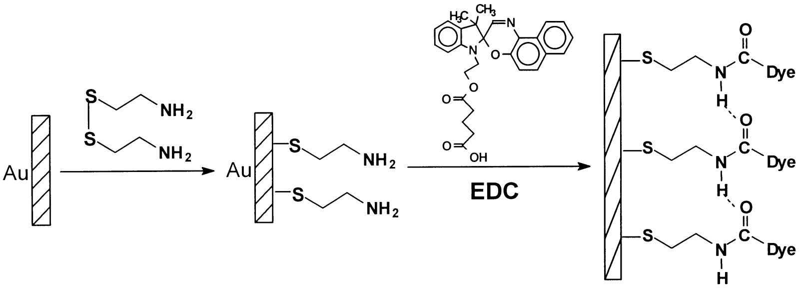


Fig. 1. Plots of $\lambda_{max}$ (nm) vs. $E_T$ value for spiroxazine dye **8** in various solvents.



Scheme 2. Stepwise organization of the spiroxazine dye **8** monolayer on gold layer.

the preferred reagent for this amide coupling reaction [22].

The spiroxazine exhibited photochromism insofar as the colourless species turned blue or violet upon uv-irradiation and was bleached upon visible light irradiation or heating. Fig. 2 shows the visible absorption spectrum of a cast film of the spiroxazine dye **8**; the change of absorbance was recorded by scanning at various time intervals. Upon irradiation with 365 nm light, a new absorption peak appeared at around 620 nm; the new band is ascribable to the open-ring form of **8**. The photogenerated open-ring form was thermally stable.

The bulk transmission (KBr pellet) IR spectra of spiroxazine **8** is shown in Fig. 3a. The intense bands at 2923 and 2852 cm$^{-1}$ can be assigned to $CH_2$ asymmetric and symmetric stretching modes of the hydrocarbon chains and the 2960 cm$^{-1}$ band is the $CH_3$ asymmetric stretching mode. These frequencies are in agreement with those reported by other workers [23,24].

It is well known that low frequencies of the $CH_2$ asymmetric (~2920 cm$^{-1}$) and symmetric (~2850 cm$^{-1}$) stretching modes are characteristic of regular, planar zigzag ('all-*trans*') structures, with no gauch-defects (i.e. *cis* C–C bonds). Thus, the $CH_2$ stretching bands at 2923 and 2852 cm$^{-1}$ indicate that the hydrocarbon chains of the spiroxazine dye **8** assume a near *trans*-zigzag conformation in the solid state. The two most characteristic features of

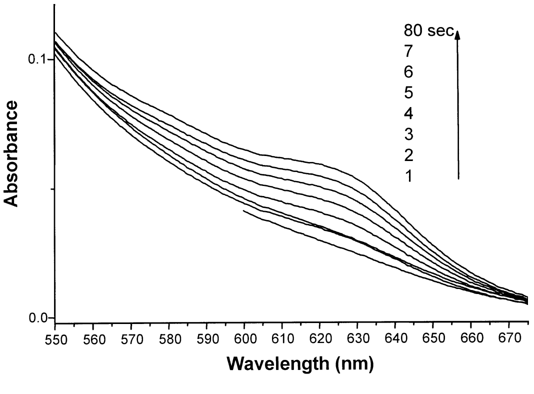


Fig. 2. Photo-induced spectral changes in the visible absorption bands of film exposed to light (365 nm).

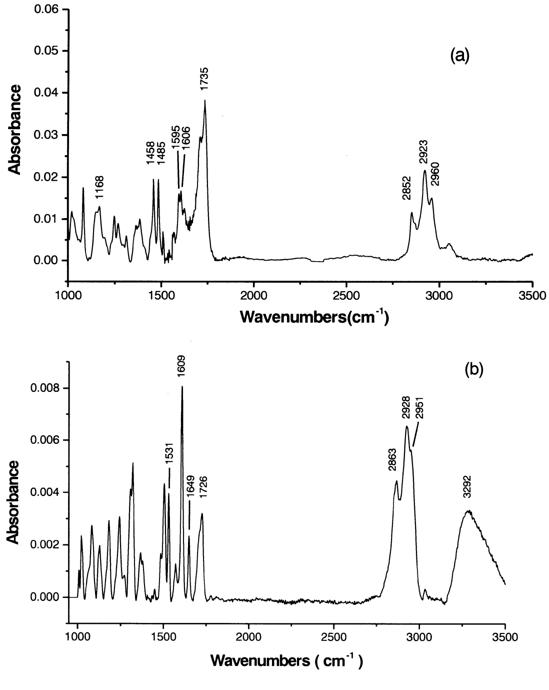


Fig. 3. Infrared transmission spectra of spiroxazine dye **8** in KBr (a) and RA spectra in SAM (b).

the dye are the strong C=O, which appeared at 1735 $cm^{-1}$ and the C–O stretching absorption which appeared at 1168 $cm^{-1}$. The peaks observed at 1458–1485 $cm^{-1}$ and at 1595–1606 $cm^{-1}$, are characteristic peak assignments which can be attributed to aromatic C=C stretching. Fig. 3b shows the IRRA spectra of dye **8** in the SAM state. The FTIRRAS in Fig. 3b shows strong NH stretching (amide A) at 3292 $cm^{-1}$, C = O stretching (amide I) at 1649 $cm^{-1}$ and NH in-plane bending (amide II) at 1531 $cm^{-1}$. The bands of 2928 and 2863 $cm^{-1}$ can be assigned to the asymmetric C–H stretching mode of a methylene group and the symmetric C–H stretching mode of a methylene group, respectively. Also, the C–H asymmetric stretching band of the $CH_3$ group is observed at 2951 $cm^{-1}$.

It is well known that the peak positions of methylene stretching bands are strongly affected by molecular conformation and vary significantly from the solid to the SAM states. The peak positions of the SAM appear at higher frequencies [2928 $cm^{-1}$: $\nu_{as}$ ($CH_2$), 2863 $cm^{-1}$: $\nu_s$ ($CH_2$)] than that of the solid. The bands for the SAM suggest that the molecules adopt the gauche conformation in the hydrocarbon chains. The peak intensity of the $CH_2$ bands depends upon the surface concentration, orientation and conformation of the adsorbed molecule. With an accurate knowledge of the directionality of vibrational transition dipole moments, the determination of the orientation of molecules with respect to the surface is simplified by the effect of the metal surface selection rule.

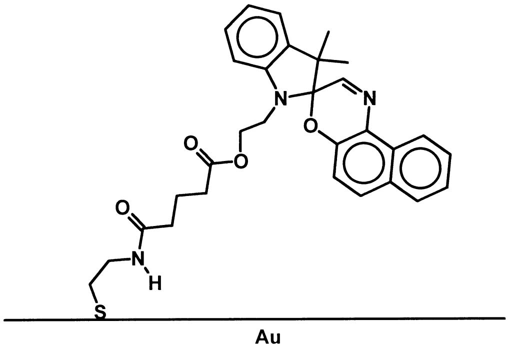


Fig. 4. Schematic representation of the molecular orientation of the spiroxazine dye **8** on a gold layer.

The *p*-polarized light used in the FTIRRAS experiments only interacts with vibrational modes perpendicular to the sample surface. If the alkyl backbone is perpendicular to the surface (a tilt angle of 0°), the C–H bonds would be nearly parallel to the surface and so not absorb much *p*-polarized light. Alternatively, a tilt angle greater than zero would orient the C–H bonds perpendicular to the surface and thereby increase the absorbance (peak area). It is of interest that the intensities of the bands due to the $CH_2$ asymmetric and symmetric stretching modes become much stronger in the RA spectra (Fig. 3b) than in the transmission spectra (Fig. 3a).

According to the surface selection rule, the results suggest that the hydrocarbon chains are inclined normally from the surface. It may be concluded from the intensities and positions of the CH stretching mode that the spiroxazine dye **8** in the SAM assumes a gauche conformation and is tilted considerably from the surface normal in the SAM (Fig. 4).

## Acknowledgements

The authors wish to acknowledge the financial support of the Korea Research Foundation made in the Program year of 1998.

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