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Surface plasmon resonance spectroscopy on the interaction of a self-assembled monolayer with linear hydrocarbon such as pentane, hexane, heptane and octane

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Abstract

Surface plasmon resonance study on the interaction of a self-assembled spiroxazine monolayer with linear hydrocarbon solvents such as pentane, hexane, heptane and octane has been studied. The resonance angle shift of the SAM of spiroxazine dye 6, 13 increased with decreasing viscosity: the order of relative resonance angle shift was as follows; pentane > hexane > heptane > octane.

Keywords: Self-assembled monolayer; Spiroxazine; Surface plasmon resonance; Viscosity

1. Introduction

Surface plasmon resonance (SPR) is one of the promising optical techniques for chemical sensing, and SPR configuration systems such as immunoassay [1], liquid [2], gas [3] and thin films [4] have been reported.

SPR is an optical process in which light satisfying a resonance condition excites a charge-density wave that is propagating along the interface between a metal, such as silver or gold, and a dielectric material. When the light is polarized with its electric field in the plane of incidence, the field causes collective oscillations of the electrons in the metal layer and results in bunching of these electrons.

At the surface plasmon resonance angle, the energy of the metal surface coincides with the incident photon and the charge density wave. The photon energy is then transferred to the surface plasmon waves, which result in energy loss from reflected intensity.

This phenomenon can be observed as a sharp dip in the reflected light intensity. Outside the

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metal, an evanescent electric field exists. This evanescent wave is part of the internally reflected light beam and partially penetrates into the lower refractive index medium. The evanescent wave can interact optically with compounds that are close to the surface or at the surface. Changes in the optical properties of this region will influence the SPR angle, this accounts for the usefulness of SPR optical switching.

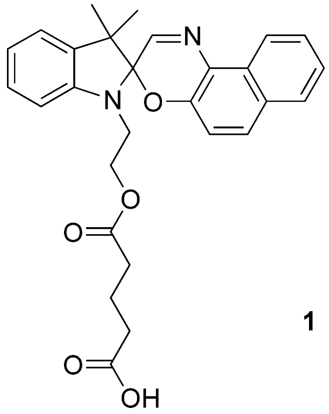
Recently, photochromic materials have gained much attention, and they now constitute an active research area because of their tremendous importance in biological phenomena and in their potential applications in the areas of linear and nonlinear optics [5].

Although the photochromism of spiropyrans has been extensively studied [6,7], little work has been carried out on spironaphthoxazine dyes. These two class of compounds are similar in many respects. However, the replacement of the benzopyran ring by a naphthoxazine ring result in spironaphthoxazine having the advantage of greatly improved resistance to prolonged UV irradiation, which confers a much more commercial importance of them [8].

Ultrathin organic films are of considerable interest because of their potential technological applications in the fields of surface coatings, sensors and optoelectronics [9]. These films are commonly formed using Langmuir–Blodgette (LB) deposition or self-assembly techniques (SAMs) based on chemisorption. The monolayers prepared from sulfur containing species, such as thiols and disulfides, at gold surfaces have been especially well studied because of their tendency toward forming quasi-crystalline monolayers with well-defined structures [10].

Although most of the studies have been accomplished for SAMs without functional groups, such as alkanethiolate SAMs, increasing interest has been directed toward SAMs containing chromophores for optical application [11]. We have previously reported the synthesis and self-assembly of the photochromic spiroxazine dye **1**-containing alkanethiol with an amide group incorporated into the backbone [12–14].

In this paper, we report the preparation and properties of a photochromic spiroxazines **6,13**-containing alkanethiol monolayer on gold. We also reported the photo-induced switching of a SAM of spiroxazines **6**, **13** deposited gold using linear hydrocarbon solvent such as pentane, hexane, heptane and octane, using SPR spectroscopy.



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2. Experimental

2.1. Characterization of products

Melting points were determined using an Electrothermal IA900 and are uncorrected. Elemental analysis 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. ^{1}H-NMR spectra were recorded on Varian Unity Inova 400 MHz FT-NMR spectrometer with TMS as internal standard.

2.2. Intermediate 4

Compound **4** was prepared from 1, 3, 3-trimethyl-2-methyleneindoline and 1-nitroso-2, 7-dihydroxy naphthalene **3** according to the method described in Refs. [15,16]. Yield 3.23 g (23.5%), m.p. 211.5–214 °C. ^{1}H-NMR ($CDCl_3$): δ 7.76 (2H, m), 7.67 (1H, d, $J=8.8$ Hz), 7.62 (1H, d, $J=8.8$ Hz), 7.19 (1H, m), 7.12 (1H, $J=7.3$ Hz), 6.99 (1H, m), 6.92 (1H, m), 6.77 (1H, d, $J=8.8$ Hz), 6.62 (1H, d, $J=7.8$ Hz), 2.72 (3H, s), 1.29 (6H, m) Elemental analysis: C; 76.02, H; 5.93, N; 8.10 $C_{22}H_{20}N_2O_2$ requires : C; 76.72, H; 5.85, N; 8.13.

2.3. Spiroxazine dye **6**

Compound **4** (2.4 g, 6.98 mmol), glutaric anhydride (0.8 g, 7.01 mmol) in bezene (100 ml) was refluxed for 36 h. The precipitated solid was filtered and dried. Recrystallization from *n*-hexane afford 0.73 g (22.7%) of the spiroxazine **6**. m.p. 188–191 °C. ^{1}H-NMR ($CDCl_3$): δ 8.22 (1H, d, J = 2.2 Hz), 7.75 (1H, d,d = 8.8 Hz), 7.22 (1H, s), 7.65 (1H, d, J = 8.9 Hz), 7.22 (1H, d, J = 8.9 Hz), 7.13 (2H, m), 6.98 (1H, d, J = 8.8 Hz), 6.90 (1H, m), 6.58 (1H, d, J = 4.8 Hz), 2.76 (5H, m), 2.58 (2H, t, J = 7.2 Hz), 2.14 (2H, m), 1.35 (3H, s), 1.34 (3H, s) Elemental analysis: C; 70.39, H; 5.80, N; 5.92 $C_{27}H_{26}N_2O_5$ requires: C; 70.73, H; 5.72, N; 6.11.

2.4. Intermediate **8**, **9**, **10** and **12** [17]

2.4.1. Compound **8** (5-methoxy-2, 3, 3-trimethyl indoline)

A solution of 4-methoxy phenylhydrazine hydrochloride **7** (10 g, 0.057 mol) and methyl isopropyl ketone (6.1 ml, 0.057 mol) and ethanol was refluxed for 4 h. After filteration, the solvent was evaporated to give product **8**. This product was used directly in the following step without further purification.

2.4.2. Compound **9** (5-hydroxy-2, 3, 3-trimethyl indolenine)

A solution of 5-methoxy-2, 3, 3-trimethyl indolenine (10 g, 0.057 mol) in 30 ml of methylene chloride was cooled in an ice bath. Boron tribromide (11 ml, 0.11 mol) in 20 ml methylene chloride was added dropwise while stirring. The mixture was left at room temperature overnight and neutralized by saturated sodium carbonate solution. Methylene chloride layer was separated, dried, solvent was evaporated to yield 7.67 g (84%) of brown solid. ^{1}H-NMR ($CDCl_3$): δ 7.34 (1H, d, J = 8.24 Hz), 6.82 (1H, d, J = 2.44 Hz), 6.77 (1H, m), 2.25 (3H, s), 1.28 (6H, s). Elemental analysis: C; 74.89, H ; 7.55, N; 7.56 $C_{11}H_{13}NO$ requires: C; 64.98, H; 7.48, N; 7.99. m/z (M^+)175.

2.4.3. Compound 10 (5-hydroxy-1, 2, 3-tetramethyl-3H-indolenium iodide)

To 3 g (0.017 mol) of 5-hydroxy-2, 3, 3-trimethyl indolenine **9**, 6 ml of methyl iodide were added. The mixture was refluxed overnight, the precipitated product was filtered, washed with benzene and recrystallized from ethanol to yield 2.7 g (45%) of brown soild. ^{1}H-NMR($CDCl_3$): δ 7.60 (1H, d, J = 8.28 Hz), 7.18 (1H, d, J = 2.36 Hz), 7.06 (1H, m), 3.96 (3H, s), 3.37 (3H, s), 1.54 (6H, s). Elemental analysis: C; 45.82, H; 5.09, N; 4.19 $C_{12}H_{16}NOI$ required: C; 45.44, H; 5.08, N; 4.42.

2.4.4. Compound **12** (5-hydroxy spiroxazine)

Compound **10** (5.53 g, 0.0174 mol) and nitrosonaphthol **11** (3.1 g, 0.018 mol) were dissolved in 150 ml of absolute ethanol in the presence of 1.48 g(0.0174 mol) of piperidine. After the reaction mixture was refluxed for 3 h, solvent was evaporated. Recrystallization from *n*-hexane affored 0.8 g (13.3%) of the compound **12**.

2.5. Spiroxazine dye **13**

Spiroxazine dye **13** was synthesized in a similar way to that described for spiroxazine dye **6**. Material was purified by recrystallization from ethylacetate/chloroform (1:1). Yield 0.39 g (37%), m.p. 181 °C. ^{1}H-NMR ($(CD_3)_2SO$): δ 8.5 (1H, d, J = 8.3 Hz), 7.9 (1H, s), 7.8 (2H, dd, J = 7.0 and 8.6 Hz), 7.6 (1H, m), 7.4 (1H, m), 7.1 (1H, J = 8.8 Hz), 6.6 (2H, m), 6.4 (1H, d, J = 7.7 Hz), 2.7 (2H, m), 2.6 (3H, s), 2.3 (2H, d, J = 7.0 Hz), 2.2 (2H, m), 1.2 (6H, m). Elemental analysis: C; 70.7, H; 6.2, N; 6.0 $C_{27}H_{26}N_2O_6$ requires: C; 70.73, H; 5.72, N; 6.11.

2.6. Surfaceplasmon resonance (SPR) measurements

Measurements were performed with a home-made Kretschmann configuration apparatus (Fig. 1). Details of the preparation of the spiroxazine-containing alkanethiol self-assembled monolayer on gold for SPR measurements can be found elsewhere [12, 14]. A slide glass with a spiroxazine **6**,**13**-containing SAM formed on a gold surface and prism (n = 1.515, Sigma, BK 7) were loaded on a computer controlled rotating stage. Optical contact between the prism and slide glass was achieved by a refractive index matching fluid (n_D = 1.515–1.517, Merck). The *p*-polarized He–Ne

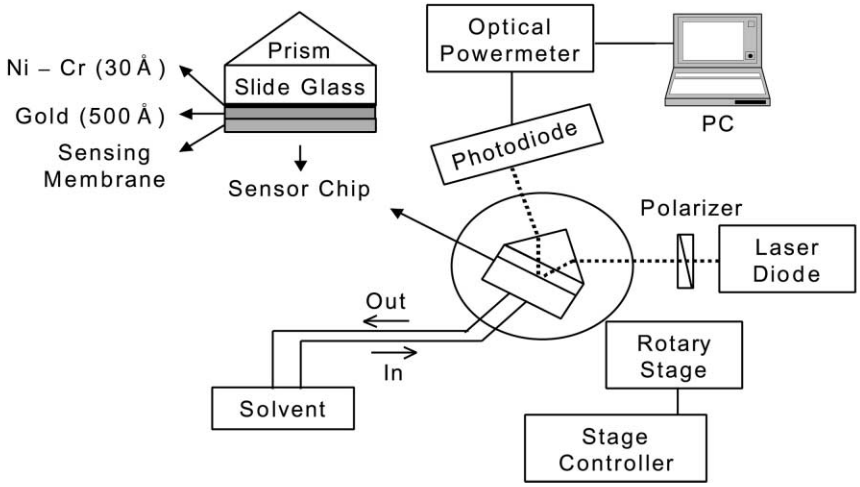


Fig. 1. Schematic diagram of SPR sensor system.

laser at 670 nm was used as probe beam. Reflected intensity via prism was measured with the photodiode detector (Ando Electric Co. Ltd., AQ-1976) and optical multimeter (Ando Electric Co. Ltd., AQ-1135E). The angle was regulated by the automatic-monorized rotary stage controller with a resolution of 0.004°. A high-pressure mercury lamp (Ushio, SP3–250D) was used as the UV radiation source and was calibrated with a monochromator at 366 nm. In order to investigate the photochromic properties of the SAMs, the UV light source was switched and radiated the SAMs layer. All solvents were pumped into the sample cell.

2.7. Infrared measurements

FTIR-RAS (Fourier transform infrared reflection absorption spectroscopy) measurements were carried out using a Nicoler Magma-IRTM550 spectrometer. A narrow-band HgCdTe detector, cooled with with liquid nitrogen, was used to detect the reflect light. For the IR-RAS measurement, GRASEBY SPACE grazing angle reflectance accessory equipped with a polarizer was used at 80 °C. All spectra were collected with 2 cm^{-1} resolution. To minimize the signal-to-noise ratio, several hundred scans were made.

3. Results and discussion

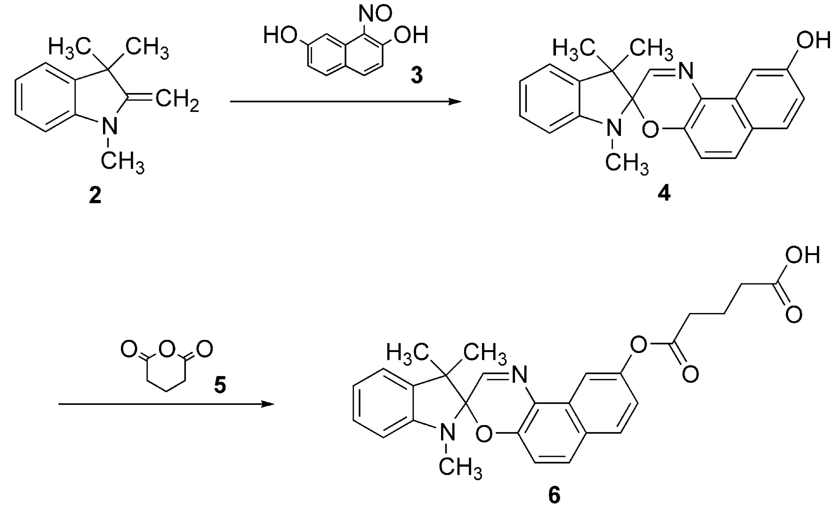
3.1. Synthesis

The synthetic route to the spiroxazine **6** is outlined in Scheme 1. The reaction of Fisher's base **2** with nitrosodihydroxynaphthalene **3** gave the compound **4** in 23.5% yield. The reaction of compound **4** with glutaric anhydride **5** gave spiroxazine **6** in 22.7% yield. Spiroxazine **13** was prepared successfully according to the procedure shown in Scheme 2.

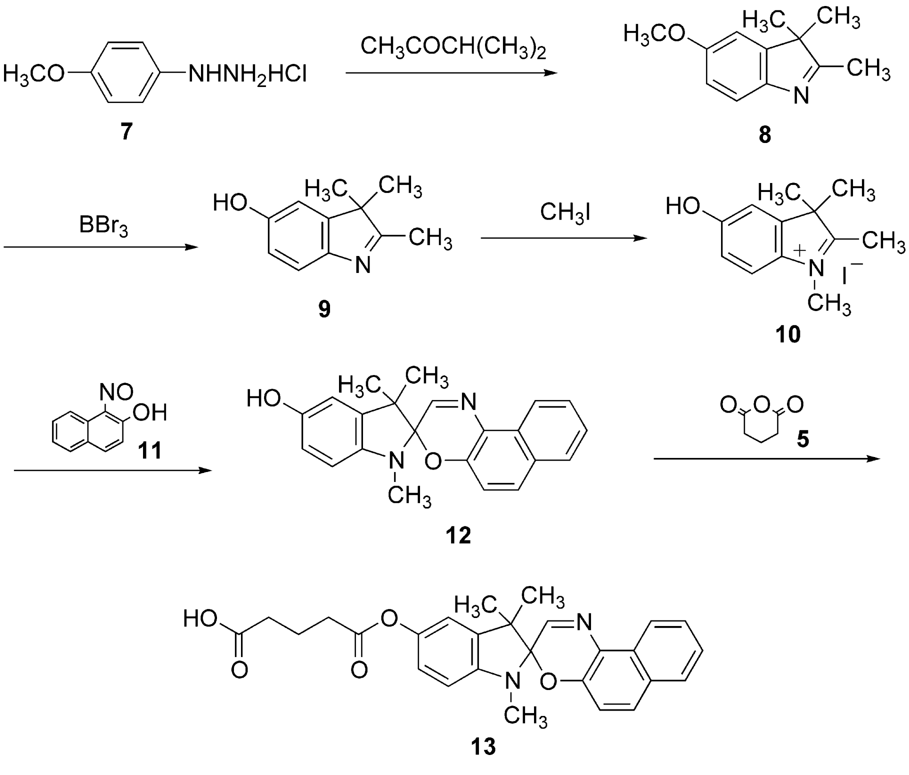
3.2. Monolayer

A monolayer was assembled on Au as outlined in Scheme 3. A cystamine monolayer was first assembled on Au. Spiroxazine dye **6**, **13** were coupled to the base monolayer using a small amount of 1-ethyl-3-(3-(dimethylamino)propyl)-carbodiimide (EDC) as recently described [18,19]. Over the years, EDC has emerged as the preferred reagent for this amide coupling reaction [20].

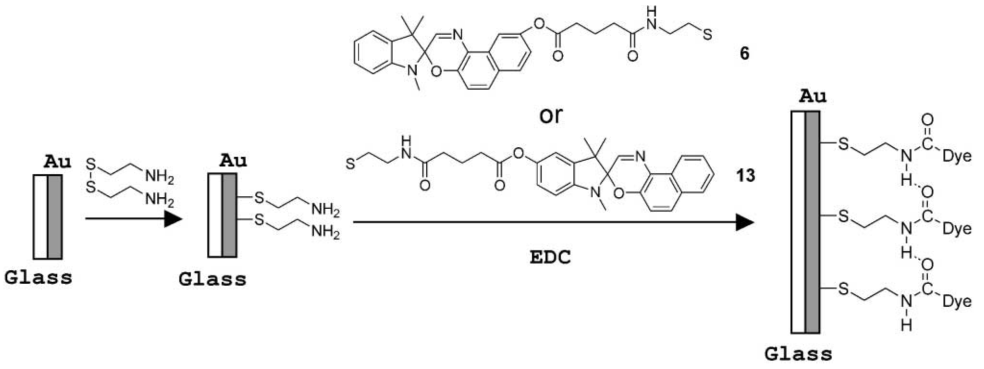
Fig. 2 shows the IRRA spectra of dye **6** in the SAM state. The FTIR RAS in Fig. 2 shows strong NH stretching (amide A) at 3163 cm^{-1}, C=O stretching (amide I) at 1668 cm^{-1} and NH in-plane



Scheme 1.



Scheme 2.



Scheme 3. Stepwise organization of spiroxazine dyes monolayer on an Au layer.

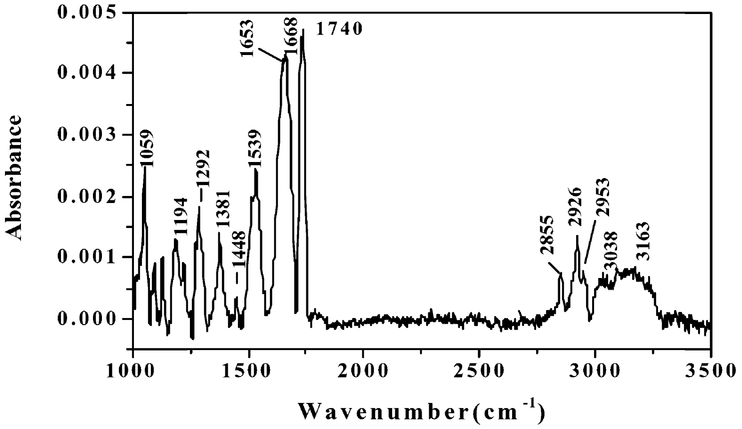


Fig. 2. FTIR-RAS spectra of spiroxazine **6** SAM.

bonding (amide II) at 1539 cm^{-1}. The bands at 2926 and 2855 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 bond of the CH_3 group in observed at 2953 cm^{-1}.

The stepwise chemical assembly of a spiroxazine **6** monolayer on gold was performed by covalent linkage to a cystamine-monolayer-modified gold surface.

SPR is a resonance phenomenon in which surface plasmon waves are excited at a metal dielectric surface, as illustrated in a classical Kretschmann configuration in Fig. 3.

In the SPR method, the resonance angle is very sensitive to variations of the medium outside the metal film. The observed resonance angle shift induced by UV irradiation can be rationalized by the formation of the photoinduced ring opened merocyanine form. Figs. 4 and 5 show the relative resonance angle shift of SAMs photochromic spiroxazine **6** and **13** before and after exposure to UV (366 nm) radiation under different solvent, respectively where θ_0 is the resonance angle before irradiation, θ_t is the resonance angle at any time after irradiation, θ_s is the resonance angle after 100 min irradiation. The observed resonance angle shift induced by UV irradiation can be rationalized by the formation of the photoinduced ring opened merocyanine form. The viscosity (n/m Pa s) of solvents used in this study were 0.24 (pentane), 0.31 (hexane), 0.42 (heptane) and 0.51 (octane). As shown in Figs. 4 and

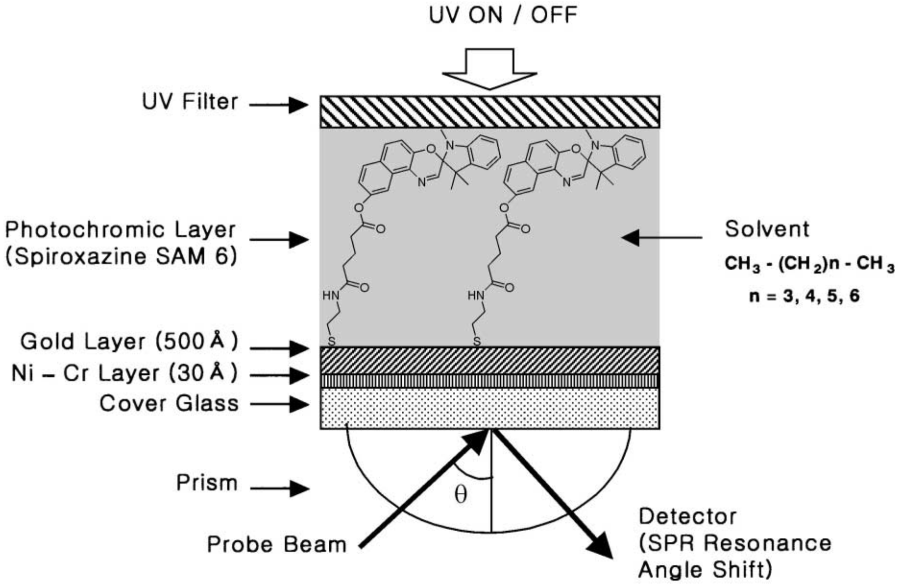


Fig. 3. Schematic diagram of SPR sensor chip for examing solvent effect.

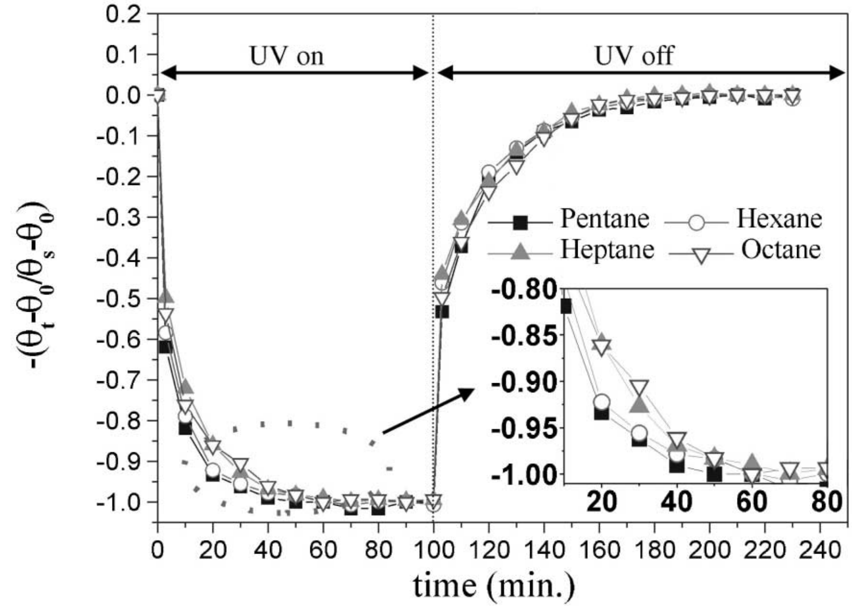


Fig. 4. Relative angle shift of spiroxazine **6** SAM under UV on/off.

5, the relative resonance angle shift of the monolayer increases markedly upon decreasing viscosity of the solvents; the order of relative resonance angle shift was as follows: pentane > hexane > heptane > octane.

Fig. 6 shows the changes in relative reflectivity, $(R_t-R_0)/(R_s-R_0)$, in response to UV-on and UV-off state where R_o is the reflectivity before irradiation, R_t the reflectivity at any time t after irradiation, R_s the reflectivity after 30 min irradiation.

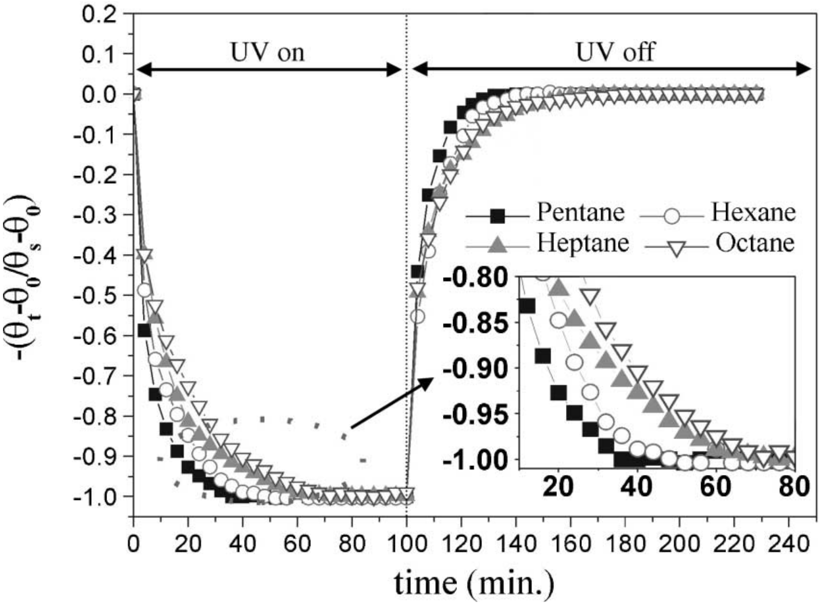


Fig. 5. Relative angle shift of spiroxazine **13** SAM under UV on/off.

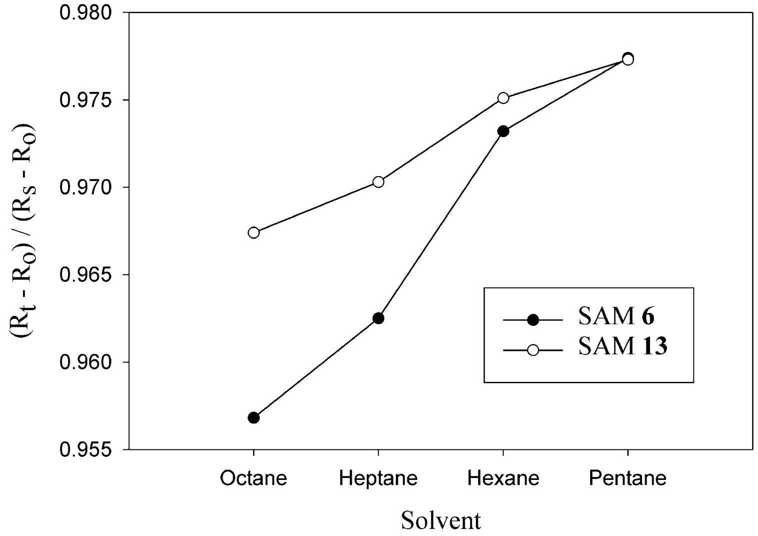


Fig. 6. The relative reflectivity at specific angle with the maximum reflectance shift by UV irradiation.

Rapid online monitoring of these changes is possible if one records the reflected intensity after 30 min irradiation ; 72.24° in pentane, 73.0° in hexane, 74.48° in heptane and 78.08° in octane for spiroxazine **6** and 68.4° in pentane, 71.8° in hexane, 74.48° in heptane and 78.0° in octane for spiroxazine **13**. As shown in Fig. 6, the relative reflectivity of the monolayer increases markedly upon decreasing viscosity of the linear hydrocarbon solvent.

Acknowledgements

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