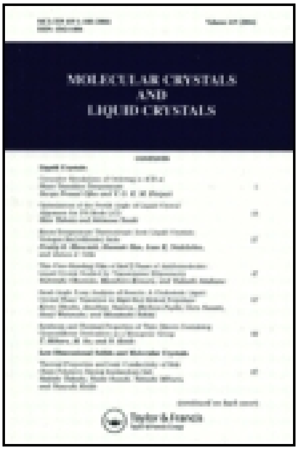


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Reflection Spectroscopy of Merocyanine Self-assembled Monolayer on a Gold Substrate

K. Tsuboi [a], K. Kajikawa [a], N. Hamada [a], K. Fujita [b], M. Hara [b], H. Sasabe [b], W. Knoll [b], K. Seki [a] & Y. Ouchi [a]

[a] Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho Chikusa-ku, Nagoya, 464-8602, Japan

[b] Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), Hirosawa 2-1, Wako, Saitama, 351-0198, Japan

Version of record first published: 24 Sep 2006

To cite this article: K. Tsuboi, K. Kajikawa, N. Hamada, K. Fujita, M. Hara, H. Sasabe, W. Knoll, K. Seki & Y. Ouchi (1998): Reflection Spectroscopy of Merocyanine Self-assembled Monolayer on a Gold Substrate, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 322:1, 191-196

To link to this article: http://dx.doi.org/10.1080/10587259808030222

Mol. Cryst. Liq. Cryst., Vol. 322, pp. 191–196
Reprints available directly from the publisher
Photocopying permitted by license only

Reflection Spectroscopy of Merocyanine Self-assembled Monolayer on a Gold Substrate

K. TSUBOI[a], K. KAJIKAWA[a], N. HAMADA[a], K. FUJITA[b], M. HARA[b],
H. SASABE[b], W. KNOLL[b], K. SEKI[a], and Y. OUCHI[a]

[a]Department of Chemistry, Graduate School of Science, Nagoya University; Furo-cho Chikusa-ku, Nagoya 464-8602, Japan; [b]Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), Hirosawa 2-1, Wako, Saitama 351-0198, Japan.

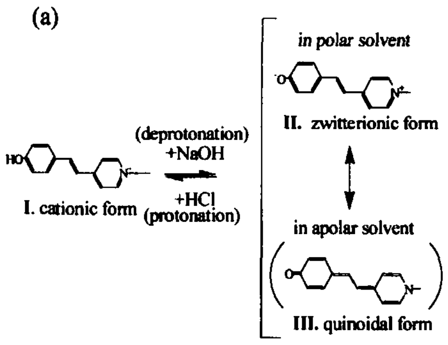
Received 6 April 1998; accepted 26 April 1998

Isomerization of merocyanine chromophores in a self-assembled monolayer (SAM) on a gold substrate was examined by means of visible-UV reflection spectroscopy. Anomalous peaks and/or dips observed in the spectra were ascribed to the loss of the metallic character of gold at the wavelength region shorter than 500nm. Spectral simulations based on the Lorentz oscillator model revealed that the merocyanine SAM undergoes isomerization even in a densely packed monolayer.

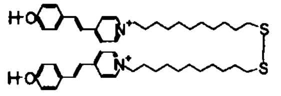
Keywords: self-assembled monolayer, solvatochromism, merocyanine

INTRODUCTION

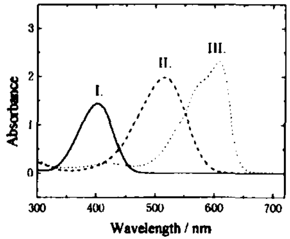
1-Methyl-4-(4-hydroxystryl)pyridinium bromide is a merocyanine dye which isomerizes with the change of environmental conditions, such as pH and the solvent polarity[1,2]. Figure 1(a) shows the isomerization diagram of this merocyanine dye. In acidic solutions this dye is in a cationic form (I). It is in a zwitterionic form (II) in basic solutions of a polar solvent, while it is in a quinoidal form (III) in basic solutions of an apolar solvent. As shown in Fig. 1(c), each form shows a characteristic absorption band. Many works have been performed on this kind of solvatochromism of such merocyanine dye[1,2,3]. In particular, the large hyperpolarizability of the zwitterionic form draws much attention to this compound as a material for nonlinear optical devices[3].



Isomerization diagram of merocyanine



(b) Merocyanine derivative



(c) Absorption spectra of the merocyanine derivative in variouse solvents

FIGURE 1 Isomerization diagram and corresponding absorption spectra for merocyanine and merocyanine derivatives

We have already reported the synthesis of the disulfide in Fig. 1(b) with two long alkyl chains derived from this merocyanine dye for fabricating a self-assembled monolayer (SAM) with the merocyanine chromophore (Mero-labled-SAM)[4]. Surface plasmon spectroscopy (SPS) and X-ray photoelectron spectroscopy (XPS) confirmed that this disulfide forms SAM on a gold substrate[4]. However their visible reflection spectra were too complicated to clarify their forms, because anomalous peaks and/or dips were observed in the spectra. This complication was ascribed to the fact that the refractive index of gold has an anomaly in the wavelength region shorter than 500nm[7]. For making an analysis of the observed spectra of the Mero-labeled-SAM on a gold substrate, in this work we performed a model calculation on the basis of the Lorentz oscillation model. We found that the isomerization occurs even in the densely-packed-monolayer.

EXPERIMENTAL

The reflection spectra were measured in the wavelength region of 300 to 700 nm by a system with a multichannel analyzer (MCPD-1000: Otsuka Electronics). The Mero-labeled-SAM was deposited on a gold thin film of 300nm evaporated on a glass substrate, and was located in a petri dish filled with ethanol as shown in an inset of Fig. 3(a). The light was guided by an optical fiber normal to the surface of the substrate. The surrounding condition was changed by adding HCl or NaOH in the solvent. Spectroscopic ellipsometry was carried out with a VASE 32 ellipsometer (J. A. Woollam Co., Inc) to obtain the refractive index of the evaporated gold substrate as a function of the wavelength. Reflection spectra were simulated for a three-layer systems (Fig. 2). The medium 1 corresponds to ethanol of a refractive index, 1.36. The medium 2 is the film with an absorbing character, which corresponds to the Mero-labeled-SAM. By assuming that the susceptibility, $\chi(\omega)$, of this film for the light of an angular frequency ω follows the Lorentz oscillation model, it is described as

$$\chi(\omega) = N\frac{fe^2}{\varepsilon_0 m}\frac{1}{\omega_0^2 - \omega^2 - i\omega\Gamma} \tag{1}$$

where f is the oscillator strength, m and e are the mass and charge of electron, N the number density, ω_0 the resonance frequency, and Γ the damping constant. The medium 3 corresponds to evaporated gold substrate, whose refractive index is obtained by the spectroscopic ellipsometry.

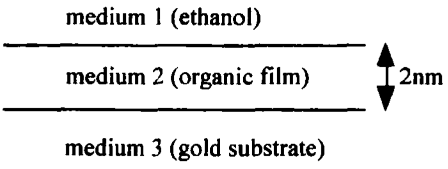


FIGURE 2 Structure of three-layer system

RESULTS AND DISCUSSION

As is illustrated in Fig. 1, the cationic, zwitterionic, and quinoidal forms show characteristic peaks located at 400nm, 520nm, and 605nm, respectively. Figure 3(a) shows the reflection spectra of the Mero-labeled-SAM prepared in the acidic and basic conditions. The spectra cannot be interpreted by direct comparison with those in Fig. 1(c). We interpret this finding that the anomaly of the refractive index of gold at around 500nm produces a ghost peak at the corresponding wavelength. To confirm this, the alkanethiolate (n-$C_{18}H_{37}SH$) SAM on gold, which has no absorption band in the region from 300nm to 700nm, showed an apparent absorption in the wavelength region shorter than 500nm, as shown in Fig. 3(b).

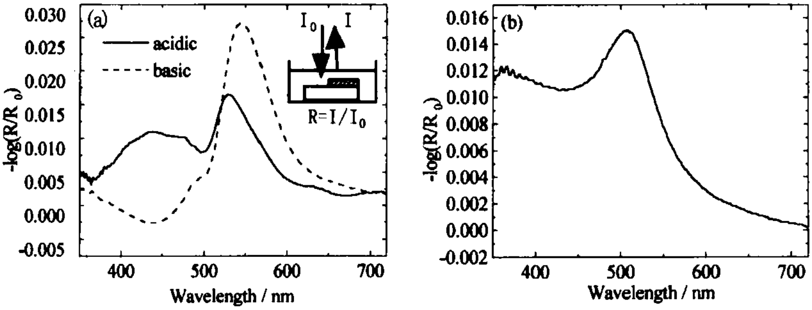


FIGURE 3 (a) Reflection spectra of Mero-labeled-SAM in ethanol
(b) Reflection spectrum of (n-$C_{18}H_{37}SH$) SAM in air

The parameters used in the spectral simulation were determined in the follow way: (1) The transmission spectrum in air of a merocyanine film, which was fabricated by simply dipping a silica plate in the ethanol solution, is shown in Fig. 4. (2) The damping constant Γ was calculated from the FWHM of the corresponding absorption band: Γ=7.9x10^{14}/sec^{-1} in the cationic form and Γ=1.26x10^{14}/sec^{-1} in the zwitterionic form. The oscillator strength f of the cationic form was estimated to be 1.4x10^{-6} from the value of the monolayer Langmuir-Blodget film of this merocyanine dye reported by Robert *et al.*[5]. The value of f for the zwitterionic form was determined to be 1.2x10^{-6} from the intensity ratio between the peaks in the absorption spectra of the protonated and deprotonated solutions. Thickness of medium 2 was estimated to be

2.0 nm from the molecular model and the result of SPS[4].

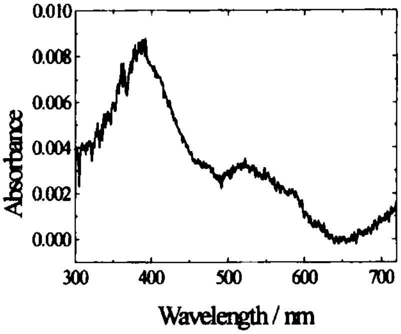


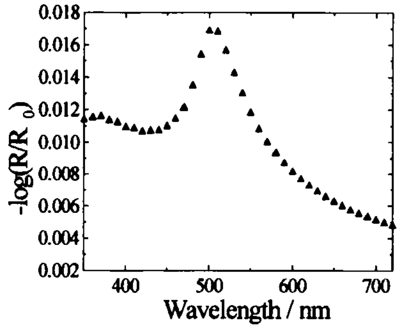
FIGURE 4 Transmission spectrum of the film of the merocyanine derivative formed on a silica plate

The refractive index of medium 2 at the frequency ω is described as

$$n(\omega)=\sqrt{\chi(\omega)+\varepsilon_\infty}+in_r \tag{2}$$

where ε_∞ is the dielectric constant at low frequency range without absorption. We used a typical value of n=1.5 for an organic material. This leads to ε_∞ =2.25. n_r is the effective damping constant of the film, which originates from the undulated structure of the SAM. This reflects the roughness of the gold surface[6]. We estimated n_r to reproduce the reflection spectrum of the alkanethiolate SAM(Fig. 3(b)), as shown in Fig. 5. The reflection spectrum cannot be well simulated without this effective damping factor n_r[7]. With the parameters described above, we could successfully simulate the observed reflection spectra (Fig. 3(a)) as shown in Fig. 6.

The absorption band at 400nm in the acidic condition appears as the dip at 350nm (solid arrow) due to the decrease of the refractive index of the real part[4]. In the basic condition, the absorption band at 520nm also appears as a dip at 450nm (dotted arrow), although the absorption peak at 530nm is a ghost due to the anomaly of the dielectric constant of gold. The spectral change observed in the wavelength region shorter than 500nm clearly indicates the presence of the absorption bands of the Mero-labeled-SAM, which is attributable to the transition between the protonated and the deprotonated zwitterionic forms.



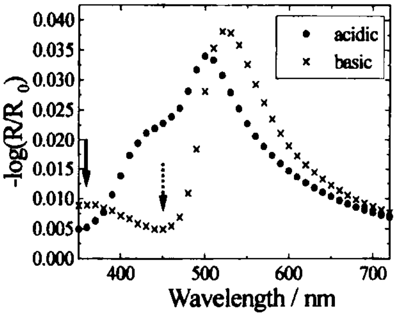


FIGURE 5 (left) Simulated reflection spectrum of $C_{18}H_{37}SH$ SAM
FIGURE 6 (right) Simulated reflection spectra of mero-labeled-SAM

CONCLUSION

We have successfully simulated the observed reflection spectra of the Mero-labeled-SAM. The results confirm that the merocyanine moiety isomerizes even in the densely packed structure of the SAM.

References

[1.] L. G. S. Brooker, G. H. Keyes, and D. W. Heseltine, *J. Am. Chem. Soc.*,**73**, 5350 (1951)

[2.] G. L. Gains, Jr., *Anal. Chem.* **48**, 450 (1976).

[3.] I. R. Giriling, P. V. Kolinsky, C. M. Montgomery, N. A. Cade, J. D. Earls, I. R. Peterson, *Opt. Commun.*, **55** ,289 (1985).

[4.] K. Fujita, M. Hara, H. Sasabe, W. Knoll, K. Tsuboi, K. Kajikawa, K. Seki, Y. Ouchi, to be submitted.

[5.] R. A. Hall, P. J. Thistlethwaite, F. Grieser, N. Kimizuka, T. Kunitake, *Langmuir*, **10**, 3743 (1994).

[6.] The roughness factor of the gold substrate is involved in dielectric constant.

[7.] K. Kajikawa, K. Tsuboi, M. Sei, K. Seki, Y. Ouchi, in preparation.