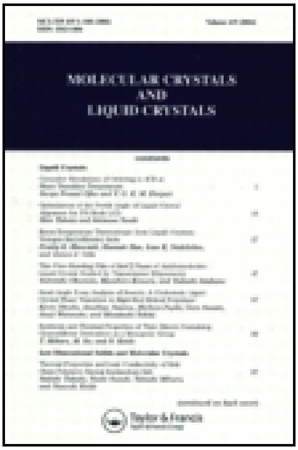

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Structure of Hybrid Langmuir-Blodgett Films of Amphiphilic Cyclodextrin and Water-Soluble Azobenzene

Mutsuyoshi Matsumoto [a] , Yoko Matsuzawa [a] , Satoshi Noguchi [b] , Hideki Sakai [b] & Masahiko Abe [b]

[a] Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan

[b] Faculty of Science and Technology, Tokyo University of Science, Noda, Japan

Version of record first published: 18 Oct 2010

To cite this article: Mutsuyoshi Matsumoto, Yoko Matsuzawa, Satoshi Noguchi, Hideki Sakai & Masahiko Abe (2004): Structure of Hybrid Langmuir-Blodgett Films of Amphiphilic Cyclodextrin and Water-Soluble Azobenzene, Molecular Crystals and Liquid Crystals, 425:1, 197-204

To link to this article: http://dx.doi.org/10.1080/15421400490506801

Mol. Cryst. Liq. Cryst., Vol. 425, pp. 197/[475]–204/[482], 2004

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490506801

Taylor & Francis
Taylor & Francis Group

STRUCTURE OF HYBRID LANGMUIR-BLODGETT FILMS OF AMPHIPHILIC CYCLODEXTRIN AND WATER-SOLUBLE AZOBENZENE

Mutsuyoshi Matsumoto and Yoko Matsuzawa
Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 5-2, 1-1-1 Higashi, Tsukuba 305-8565, Japan

Satoshi Noguchi, Hideki Sakai, and Masahiko Abe
Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda 278-8510, Japan

Amphiphilic alkylamino cyclodextrins (CDs-NH) in the Langmuir films had strong intermolecular interaction with sodium salt of p-methyl red (p-MR) in the subphase. Molecules of p-MR were incorporated in CDs-NH LB films fabricated from subphases containing p-MR. Deconvolution of the polarized UV/vis absorption spectra of α-CD-NH/p-MR LB films revealed the existence of both monomeric and H-aggregated p-MR. The AFM image of a single-layer α-CD-NH/p-MR LB film showed three-dimensional dendrites, probably due to H-aggregated p-MR. We concluded that α-CD-NH/p-MR LB films consisted of three components: (1) α-CD-NH without p-MR, (2) α-CD-NH with monomeric p-MR in the CD cavity, and (3) H-aggregated p-MR outside the CD cavity.

Keywords: AFM; azobenzene; cyclodextrin; LB film; simulation of spectrum; UV/vis absorption spectrum

Received 1 October 2003; accepted 2 February 2004

We wish to acknowledge Emeritus Professor W. Tagaki, Osaka City Univ., for providing CDs. We are also grateful to Dr. H. Tachibana, AIST, for offering p-MR.

Address correspondence to Mutsuyoshi Matsumoto, Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 5-2, 1-1-1 Higashi, Tsukuba, 305-8565, Japan. Tel.: +81-29-861-9376, Fax: +81-29-861-4669, E-mail: mutsuyoshi.matsumoto@aist.go.jp

INTRODUCTION

Langmuir-Blodgett (LB) films have been attracting considerable interest from the viewpoint of the applications to switching and memory devices, sensors and templates for the fabrication of nanoparticles [1]. Special features of LB films are thickness controllable at the molecular level, well-defined structures with controlled molecular orientation, and supramolecular structures fabricated through non-covalent bond.

We have demonstrated that various nonamphiphilic azobenzene derivatives are incorporated in the LB films of amphiphilic alkylamino cyclodextrins (CDs-NH) when prepared from equimolar mixtures of the two components [2–4]. Reversible photoisomerization of the azobenzenes incorporated in the LB films of CDs-NH has been demonstrated [5,6]. Recognition properties of CDs in the Langmuir films and the LB films have also been examined [7,8]. The monolayers of CDs-NH interacted strongly with water-soluble azobenzene in the subphase. Recognition of geometrical isomers of sodium salt of methyl red (MR) was studied. The results indicate that the CD cavity is not the only binding site for MR. However, the structures of the hybrid LB films of CD-NH and water-soluble azobenzene have not been clarified.

In this study, we will investigate the structure of hybrid LB films of CDs-NH and water-soluble azobenzene (p-MR) by the measurements of surface pressure-area isotherms, UV/vis absorption spectroscopy, simulation of the absorption spectra, IR spectroscopy and AFM.

EXPERIMENTAL

Amphiphilic CDs were synthesized as reported in the literature [8]. Molecules of p-MR were obtained by treating the corresponding acid with NaOH aqueous solution. The molecules are shown in Figure 1.

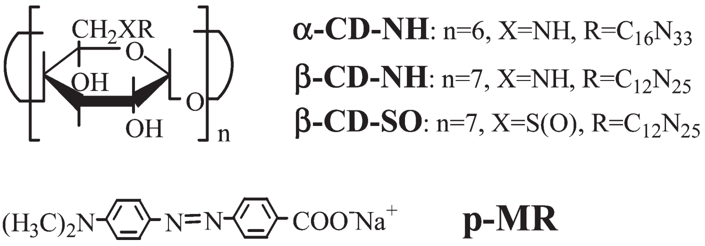

FIGURE 1 Structures of the molecules used in this study.

All the monolayer experiments were carried out on a Lauda film balance FW2. CD molecules were spread at 20°C on pure water or an aqueous subphase containing p-MR. α-CD was dissolved in a mixed solvent (chloroform/DMSO = 4/1) at a concentration of 0.1 mM. β-CDs were dissolved in chloroform at a concentration of 0.2 mM. Monolayers were transferred at 30 $\mathrm{mNm^{-1}}$ on quartz, CaF_2, evaporated Au film on glass, and mica, for UV/vis absorption spectroscopy, IR transmission spectroscopy, IR reflection-absorption (RA) spectroscopy, and AFM, respectively. UV/vis absorption spectra were measured on a varian Cary 500 Scan. The incident angle was 45° for polarized absorption spectroscopy. IR measurements were done on a Perkin Elmer Spectrum 2000 FTIR. The incident angle for RA measurements was 80°. AFM images were obtained on a Seiko SPI3800 system in a noncontact mode.

RESULTS AND DISCUSSION

Figure 2 shows surface pressure-area isotherms of CDs with variations in the concentration of p-MR in the subphase. The isotherm of β-CD-SO does not change significantly with the introduction of p-MR in the subphase.

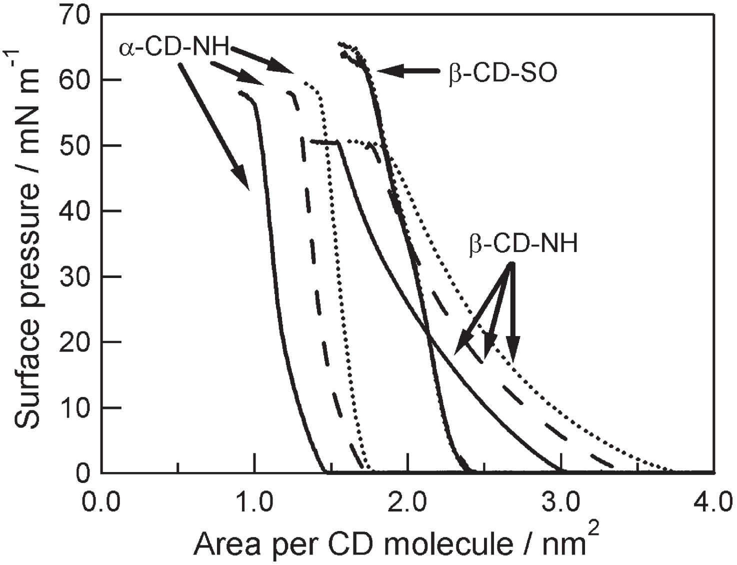

FIGURE 2 Surface pressure-area isotherms of CDs on aqueous subphases containing p-MR at 20°C. Solid lines: pure water, dashed lines: p-MR solution (10^{-6} M), dotted lines: p-MR solution (10^{-5} M).

On the other hand, the isotherms of α-CD-NH and β-CD-NH are shifted to larger area per molecule with increasing concentrations of p-MR. The results indicate strong intermolecular interaction between CDs-NH and p-MR in the subphase, probably through salt formation or hydrogen bonding.

CD monolayers with p-MR at a concentration of 10^{-6} M in the subphase were transferred onto solid substrates as LB films. UV/vis absorption spectra of the LB films were measured. Absorption bands due to p-MR were observed in the spectra of the LB films of α-CD-NH and β-CD-NH whereas such a band was absent in the spectra of the LB films of β-CD-SO. This is consistent with the surface pressure-area isotherms described above. Polarized absorption spectra of the former two LB films were measured to investigate the orientation of p-MR in the LB films. Large out-of-plane anisotropy was observed in the LB films of α-CD-NH with absorption peaks at 363 and 418 nm in the p-polarized and s-polarized spectra, respectively. This indicates that two components of p-MR with different electronic states are present in the LB films. Small out-of-plane anisotropy was observed in the polarized spectra of the LB films of β-CD-NH.

We describe a calculation method of the tilt angles and the molecular ratio of the two components based on the intensities of the absorption bands of the two components in the polarized spectra of α-CD-NH/p-MR LB films. Assume that two kinds of electronically different but chemically the same molecules with transition moment **M** are oriented in a thin film, each kind distributed uniformly with a polar angle θ_i (i = 1,2). Intensity of the absorption band (area of absorption band plotted against wavenumber) in the p-polarized spectrum Ip_i and that in the s-polarized spectrum Is_i are expressed as follows:

$$Ip_i = (1/2)kN_iE^2M^2(\sin^2\theta_i\cos^2\beta + 2\cos^2\theta_i\sin^2\beta) \tag{1}$$

$$Is_i = (1/2)kN_iE^2M^2\sin^2\theta_i \tag{2}$$

$$Is_i/Ip_i = \sin^2\theta_i/(\sin^2\theta_i\cos^2\beta + 2\cos^2\theta_i\sin^2\beta) \tag{3}$$

where k is a constant, N_i is the number of molecules of i-th component, E is the electric field vector and β is the angle of refraction [9]. Equations (1) and (2) give the following expressions:

$$N_1/N_2 = (Ip_1/Ip_2)(\sin^2\theta_2 + 2\cos^2\theta_2\tan^2\beta)/(\sin^2\theta_1 + 2\cos^2\theta_1\tan^2\beta) \tag{4}$$

$$N_1/N_2 = (Is_1/Is_2)(\sin^2\theta_2/\sin^2\theta_1) \tag{5}$$

Both of the equations yield the same value of the molecular ratio unless the first component is oriented perpendicularly in the film ($\theta_1 = 0$).

We carried out peak separation and obtained the tilt angles and the molecular ratio of the two components by the following procedures. First, we deconvoluted the p-polarized and s-polarized spectra by assuming that each of the spectra consists of two Gaussian curves. The sum of the squares of deviation was minimized by optimizing the peak positions, the peak intensities and the linewidths of the two components. Good agreement is obtained between the observed and simulated polarized absorption spectra as shown in Figure 3. Each component spectrum is also shown. Components I and II are positioned at 418 and 368 nm, respectively. Then the tilt angle θ_i was obtained by substituting the values of Is_i/Ip_i into Eq. (3). The values of θ_1 and θ_2 were calculated as 50° and 16°, respectively. These results show that component I is assigned to monomeric p-MR oriented obliquely while component II is attributed to H-aggregated p-MR oriented almost perpendicularly in the LB film. Finally the molecular ratio N_1/N_2 was obtained as 0.5/1.1 using Eqs. (4) and (5). This shows that ca. 2/3 of p-MR molecules are in the form of H-aggregate.

We calculated the molecular ratio of CD to p-MR in the LB film as follows. First, the number of α-CD-NH molecules per unit area of the LB film was obtained as 0.71 molec nm^{-2} from the molecular area at the transfer pressure in the surface pressure-area isotherm. Second, the LB film was dissolved in methanol, and the UV/vis absorption spectrum of the

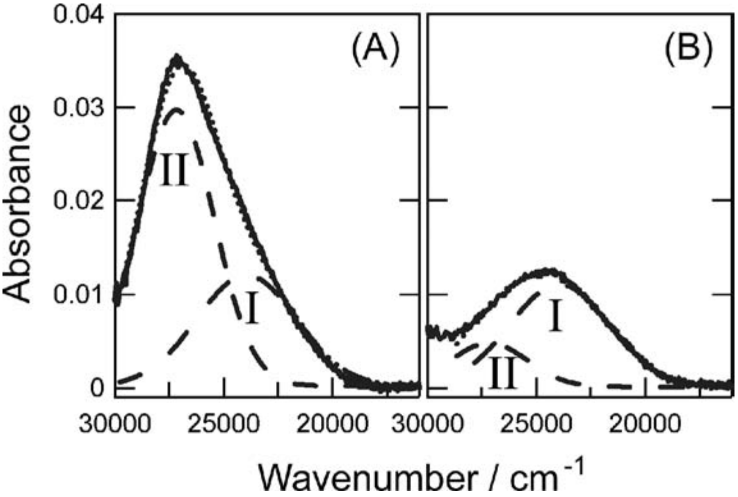

FIGURE 3 Observed and simulated polarized absorption spectra of a 5-layer α-CD-NH/p-MR LB film at an incident angle of 45°. (A): p-polarized spectra, (B): s-polarized spectra. Solid lines: observed spectra, dotted lines: simulated spectra, dashed lines: simulated spectra of the two components.

methanol solution was measured. Third, the number of p-MR molecules per unit area of the LB film was obtained as 1.2 molec nm^{-2} using a calibration curve (absorbance vs. concentration of p-MR in solution) and the transferred area of the LB film. Finally the molecular ratios are obtained as α-CD-NH : monomeric p-MR: H-aggregated p-MR = 1.0 : 0.5 : 1.1.

IR spectroscopy has been used to investigate the orientation of alkyl chains. Using the procedures described in the literature [10], the tilt angle of the alkyl chains of CD was obtained as ca. 20° in both the LB films of α-CD-NH and those of α-CD-NH/p-MR based on the intensities of the bands of $\nu a(CH_2)$ and $\nu s(CH_2)$ in the IR transmission and RA spectra. This shows that the orientation of the alkyl chains is not affected significantly by the incorporation of p-MR in the LB film.

The morphology of single-layer LB films was studied using AFM. Figure 4 shows the AFM image of a single-layer α-CD-NH/p-MR LB film. Three-dimensional structures with dendritic shapes are evident. Such dendritic structures were absent in the AFM image of a single-layer LB film of α-CD-NH. These results strongly suggest that the dendritic structures consist of p-MR, probably H-aggregated p-MR.

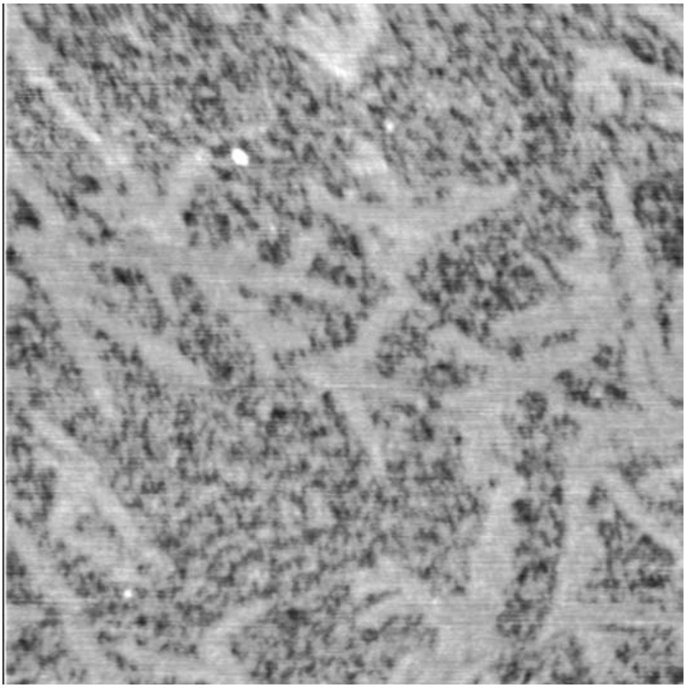

FIGURE 4 AFM image of a single-layer α-CD-NH/p-MR LB film (1 μm × 1 μm).

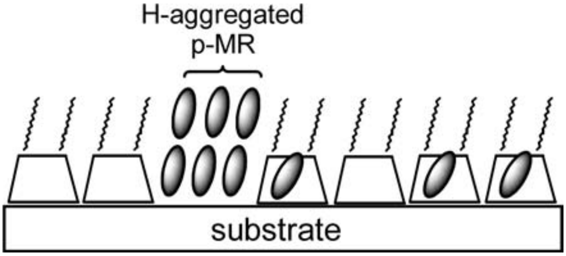

FIGURE 5 Schematic view of the structure of a single-layer α-CD-NH/p-MR LB film.

Based on the above results, we propose a model structure of a single-layer α-CD-NH/p-MR LB film. We should consider the following points: (1) each α-CD-NH can include only one molecule of p-MR, (2) α-CD-NH does not include H-aggregated p-MR, (3) hydrophilic p-MR should be positioned either near the hydrophilic portion of α-CD-NH or in domains due to phase separation, and not be buried in the hydrocarbon region, and (4) two electronic states of p-MR are not due to Davidov splitting of a single aggregate considering that one of the electronic states is assigned to monomeric p-MR. The experimental results strongly suggest that monomeric p-MR oriented obliquely in the LB film should be included in the cavity of α-CD-NH and that H-aggregated p-MR should be positioned outside the cavity of α-CD-NH, forming dendritic structures evident in the AFM image shown in Figure 4. However, we cannot exclude the possibility that some of the monomeric p-MR molecules are located outside the cavity. Figure 5 shows a schematic view of the structure of a single-layer α-CD-NH/p-MR LB film consisting of three components: (1) α-CD-NH without p-MR, (2) α-CD-NH with monomeric p-MR in the cavity, and (3) H-aggregated p-MR outside the cavity.

CONCLUSIONS

The structure of an α-CD-NH/p-MR LB film has been examined by the measurements of surface pressure-area isotherms, UV/vis polarized absorption spectroscopy, simulation of the spectra, IR spectroscopy and AFM. The results indicate that some p-MR molecules incorporated in the α-CD-NH/p-MR LB film are included in the CD cavity whereas others exist in phase-separated dendrites, forming H-aggregate outside the CD cavity. These findings will become important in applying hybrid films of CD and functional molecules to specialized purposes. Furthermore, the methodology described in this study will give a versatile tool for analyzing structures of anisotropically oriented materials where more than one electronically different species are present.

REFERENCES

[1] *J. Colloid Surf. A: Physicochem. Eng. Asp.* (Special Issue), R. Miller (Ed.), 198–200, (2002).

[2] Kawabata, Y., Matsumoto, M., Tanaka, M., Takahashi, H., Irinatsu, Y., Tamura, S., Tagaki, W., Nakahara, H., & Fukuda, K. (1986). *Chem. Lett.*, 1933.

[3] Tanaka, M., Ishizuka, Y., Matsumoto, M., Nakamura, T., Yabe, A., Nakanishi, H., Kawabata, Y., Takahashi, H., Tamura, S., Tagaki, W., Nakahara, H., & Fukuda, K. (1987). *Chem. Lett.*, 1307.

[4] Kawabata, Y., Matumoto, M., Nakamura, T., Tanaka, M., Manda, E., Takahashi, H., Tamura, S., Tagaki, W., Nakahara, H., & Fukuda, K. (1988). *Thin Solid Films*, *159*, 353.

[5] Yabe, A., Kawabata, Y., Niino, H., Tanaka, M., Ouchi, A., Takahashi, H., Tamura, S., Tagaki, W., Nakahara, H., & Fukuda, K. (1988). *Chem. Lett.*, 1.

[6] Yabe, A., Kawabata, Y., Niino, H., Tanaka, M., Ouchi, A., Takahashi, H., Tamura, S., Tagaki, W., Nakahara, H., & Fukuda, K. (1988). *Thin Solid Films*, *160*, 33.

[7] Matsumoto, M., Tanaka, M., Azumi, R., Tachibana, H., Nakamura, T., Kawabata, Y., Miyasaka, T., Tagaki, W., Nakahara, H., & Fukuda, K. (1992). *Thin Solid Films*, *210/211*, 803.

[8] Tanaka, M., Azumi, R., Tachibana, H., Nakamura, T., Kawabata, Y., Matsumoto, M., Miyasaka, T., Tagaki, W., Nakahara, H., & Fukuda, K. (1994). *Thin Solid Films*, *244*, 832.

[9] Matsumoto, M., Tanaka, K., Azumi, R., Kondo, Y., & Yoshino, N. (2002). *Langmuir*, *19*, 2802.

[10] Azumi, R., Matsumoto, M., Kuroda, S., & Crossley, M. J. (1995). *Langmuir*, *11*, 4495.