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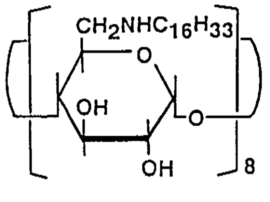
Reversible Control of Charge Transfer Interaction in the Langmuir-Blodgett Film of an Amphiphilic Cyclodextrin

Hiroyuki NIINO,[*] Hiroo MIYASAKA,[†] Akihiko OUCHI, Yasujiro KAWABATA, Akira YABE,
Hiroo NAKAHARA,[††] Kiyoshige FUKUDA,[††] Tomohiro MIYASAKA,[†††] and Waichiro TAGAKI[†††]
National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305
[††] Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338
[†††] Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558

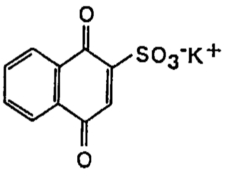
Charge transfer (CT) interaction between a naphthoquinone derivative and an amphiphilic amino-γ-cyclodextrin was regulated in host-guest Langmuir-Blodgett (LB) film upon the irradiation of UV light. The CT absorption band of the complex was reduced by the exposure to UV light, and it gradually reappeared in dark at room temperature.

In the previous papers,[1)] we have reported photoreversible *cis-trans* isomerization of azobenzene derivatives included in the Langmuir-Blodgett (LB) film of an amphiphilic cyclodextrin (CD). The cavity of CD offered favorable environment for the reversible isomerization in the LB film; the environment can be applied to various other chemical reactions in the LB film. In this paper, we have investigated a photo-induced spectral change of a charge transfer (CT) complex between a naphthoquinone derivative and an amino-CD in the LB film. It is well known that CT interaction occurs between naphthoquinones and amines.[2)] A naphthoquinone derivative as a guest molecule is expected to behave as an electron acceptor in the amino-CD LB film. It is of particular interest that CT interaction can be controlled upon photo-irradiation,[3b)] because CT complex in thin-film devices[3-5)] is important for electronic and photoelectronic applications.

The complex LB film of 1,4-naphthoquinone-2-sulfonic acid potassium salt (NQ) and octakis(6-hexadecylamino-6-deoxy)-γ-cyclodextrin ($C_{16}N$-γ-CD) was prepared as described in the previous paper.[1b,6)] The irradiation was carried out in a nitrogen atmosphere with a super high pressure mercury lamp



$C_{16}N$-γ-CD



NQ

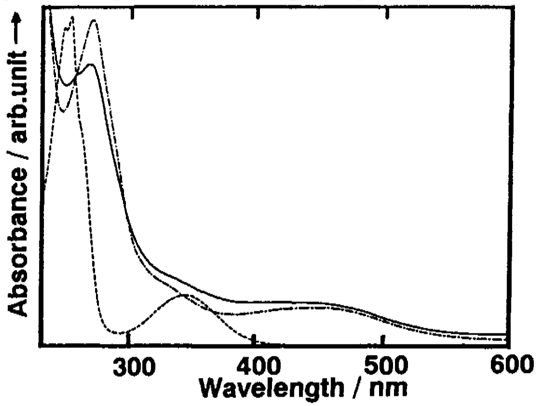


Fig.1. UV-vis spectra of NQ; (----): NQ in H_2O, (-·-·-·-): the complex with $C_{16}N$-γ-CD in H_2O, (—): the complex in LB film.

[†] Present address: Lion Corporation, Hirai, Edogawa-ku, Tokyo 132.

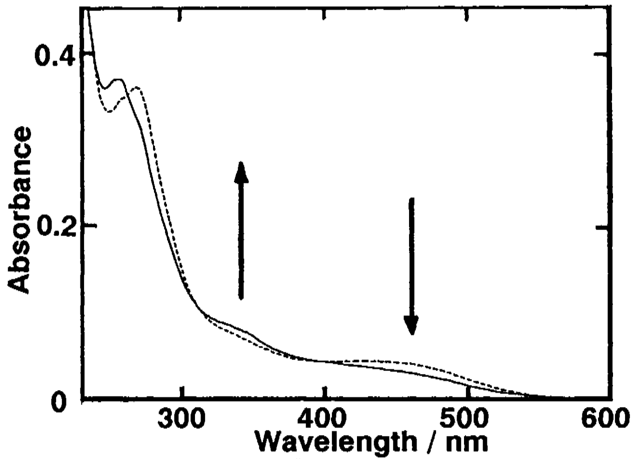


Fig.2.UV-vis spectra of **NQ** in the LB film before (---) and after (—) the exposure with UV light for 87 min.

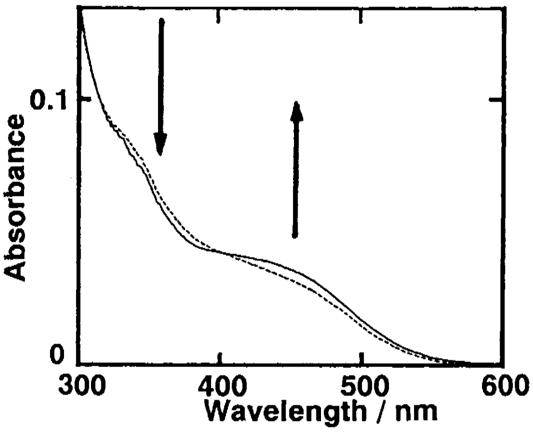


Fig.3.UV-vis spectra of **NQ** in the LB film after the photo-irradiation; (---): within 5 min, (—): after 17 days in dark.

and a filter (Toshiba: UV-D36A). The formation of the complex was confirmed by uv-visible and induced circular dichroism spectroscopies in chloroform or aqueous solution. The broad absorption band ranging from ca. 400 nm to 500 nm, which could be attributed to CT band, was observed in UV-visible spectra in both solutions (Fig.1).[7)]

In the LB film of **NQ** with $C_{16}N$-γ-CD on a quartz plate precoated with five monolayers of cadmium eicosanoate, the CT absorption band also appeared in the visible region (Fig.1). This host-guest LB film, comprised of CT complex, would exhibit characteristic properties interested in the applications of thin-film devices.

Upon irradiation of UV light, a significant decrease in the CT band was observed in the LB film (Fig.2). Other bands of **NQ** in UV region shifted similarly to those of monomer **NQ** in solution. This reduction of the CT band indicates that CT structures of the complex are changed by the irradiation. Interestingly, the CT absorption was recovered in the LB film after standing for several weeks in dark at room temperature (Fig.3). Further photo-irradiation on the recovered LB film reduced the CT absorption again. These results indicate a reversible regulation of the CT interaction by alternate operations of light on and off ; $[\ C_{16}N\text{-}\gamma\text{-}CD\cdots\cdots NQ\ ] \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} C_{16}N\text{-}\gamma\text{-}CD + NQ$. It has been found that the cavity of CD in the LB film is well suited for the control of CT interaction, although it is a slow process. In the solutions, of course, these reversible reactions were not observed. The characteristics of electric capacitance in the LB film, which is dependent upon photo-irradiation, is expected to be applied to photoelectronic materials such as optical imaging devices.

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6) The inclusion of **NQ** is supported from the value of limiting area on water ; 3.69 nm^2 (the complex of $C_{16}N$-γ-CD and **NQ**), 3.73 nm^2 ($C_{16}N$-γ-CD alone).
7) In chloroform solution of **NQ** and *N*-octadecylmethylamine (molar ratio = 1 : 10), the CT band also appeared in the same visible region.

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