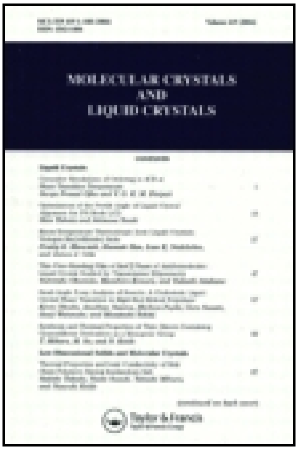

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Wei Liang [a] , Hiroo Nakahara [a] , Kiyoshige Fukuda [a] , Tatsuo Wada [b] & Hiroyuki Sasabe [b]

[a] Faculty of Science, Saitama University, Urawa, 338, Japan

[b] The Institute of Physical and Chemical Research(RIKEN), Wako, 351-01, Japan

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DIFFERENCE IN OPTICAL PROPERTIES OF MONOLAYER ASSEMBLIES OF TETRAPHENYLPORPHYRIN DERIVATIVES PREPARED BY VERTICAL DIPPING(LB) AND HORIZONTAL LIFTING(HL) METHODS

WEI LIANG[1], HIROO NAKAHARA[1], KIYOSHIGE FUKUDA[1],
TATSUO WADA[2] AND HIROYUKI SASABE[2]
1 Faculty of Science, Saitama University, Urawa, 338 Japan
2 The Institute of Physical and Chemical Research(RIKEN), Wako, 351-01 Japan

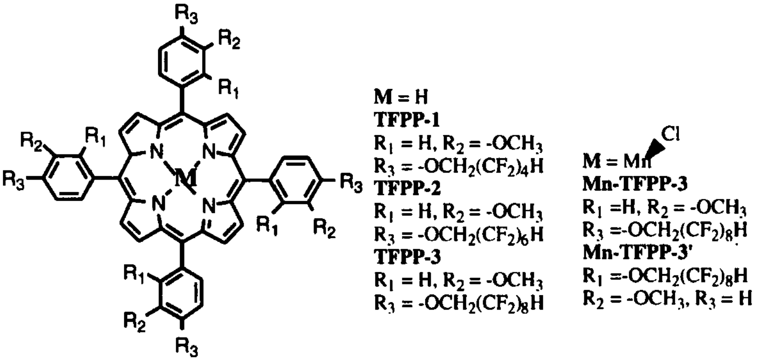
Abstract Polarized absorption and the third order nonlinear optical susceptibilities for monolayer assemblies of tetraphenylporphyrin derivatives prepared by vertical dipping(LB) and horizontal lifting(HL)methods are determined by optical third-harmonic generation(THG) measurements at a wavelength of 1907 nm. It has been found that Y-type films prepared by LB method show larger red shift in the UV-vis absorption spectra and also give larger $\chi^{(3)}$ in comparison with the X-type films prepared by HL method. This result is discussed with the difference in the electronic interaction between the porphyrin molecules in the films, induced by the transferring process.

INTRODUCTION

Porphyrins exhibit interesting properties modulated by their structural environment and molecular interactions[1], and particularly organized monolayer assemblies of porphyrins have been received a lot of attention due to their unique optical and electronic properties[2]. Recently, a great deal of effort has been devoted to Langmuir-Bloggett films of porphyrins in order to control the orientation of molecules and to enhance the photonic response for practical applications[3]. In this paper, the molecular arrangement of tetraphenylporphyrin derivatives containing four fluorocarbon chains have been examined by surface pressure-area isotherms, polarized UV-vis spectroscopy and the third harmonic generations (THG).

EXPERIMENTAL

Metal-free and manganese tetraphenyl porphyrins (TFPP) containing four fluorocarbon chains, as shown in Figure 1, were synthesized according to Lindsery's method,[4] and identified by IR, MS, NMR and elemental analysis. The monolayers were spread from the chloroform solution onto the surface of twice distilled water and the surface pressure-area (π-A) isotherms were measured by a Lauda film balance. These monolayer assemblies were built up on solid substrates at 20 mN/m by both the LB(vertical dipping) and the horizontal lifting(HL) techniques to give the Y and X-type films respectively. Polarized UV-vis spectra of the built-up films were measured by a Hitachi spectrophotometer (model 340). Third-harmonic nonlinear optical susceptibilities$\chi^{(3)}(3\omega, \omega, \omega, \omega)$ for the monolayer assemblies were obtained by using a fundamental light of 1907 nm which was converted from a 10 Hz Q-switched Nd^{3+}: YAG laser (1064 nm) by Stokes shifting through a 1 m Raman cell containing hydrogen gas. The third-harmonic light through a monochromator was detected by a photomultiplier tube, and the signal was integrated by a boxcar triggered by the laser. By the rotation of the film sample from -50° to +50° in a vacuum chamber, the THG Maker fringe was measured. The $\chi^{(3)}$ values of the porphyrin multilayers were obtained with the reference to $\chi^{(3)}$ of fused silica (1.4×10^{-14} esu.)^5.



M = H
TFPP-1
R_1 = H, R_2 = $-OCH_3$
R_3 = $-OCH_2(CF_2)_4H$
TFPP-2
R_1 = H, R_2 = $-OCH_3$
R_3 = $-OCH_2(CF_2)_6H$
TFPP-3
R_1 = H, R_2 = $-OCH_3$
R_3 = $-OCH_2(CF_2)_8H$

M = Mn Cl
Mn-TFPP-3
R_1 = H, R_2 = $-OCH_3$
R_3 = $-OCH_2(CF_2)_8H$
Mn-TFPP-3'
R_1 = $-OCH_2(CF_2)_8H$
R_2 = $-OCH_3$, R_3 = H

FIGURE 1 Chemical structures of Porphyrin TFPP and Mn-TFPP

RESULTS AND DISSCUSSION

Figure.2 shows π-A isotherms at 20°C for the metal-free TFPP's and Mn-TFPP's monolayers, TFPP-2 and 3 exhibit a transition from the liquid-expanded to condensed states and the molecular areas extrapolated from the linear part of the expanded region were 166 and 178 Å^2/molecule , whereas those of the condensed region were 118 and 128 Å^2. TFPP-1 gave the limiting area of 135 Å^2 without any transition. In contrast to these, for Mn-TFPP-3' , the surface pressure developed at the large molecular area of 215 Å^2 and on the compression of the monolayer became the condensed state with the limiting area of 146 Å^2 through the transition region. It seems to imply that the porphyrin rings for TFPP-2 and 3 are rather flat at lower pressures and tend to tilt through the transition region, while that of TFPP-1 is inclined even at lower pressures, and the larger molecular area of Mn-TFPP's seems to be ascribed to the increased hydrophilicity, which favors a flat orientation of the porphyrin ring on the water surface.

In order to determine the orientation of macrocycles in the monolayer assemblies transferred by the LB and the HL methods, polarized UV-Vis. absorption spectra were examined in comparison with the solution spectra . Figure 3 shows polarized UV-vis spectra at 45° incidence for the monolayer assemblies of TFPP-3 as a example in comparison with the solution spectra . It has been found that the spectra of the Y-type films are different from that of the X-type films. Table.1 shows the absorption maximum, the shift from the solution one and the dichroic ratio(R=Ip/Is) for porphyrin derivatives transferred by both LB and HL methods. The considerable red shift (25 nm) is observed in the Y-type film compared with that in the X-type film. The observed red-shift of the Soret band indicates that we are dealing with typical J or edge-to-edge type of aggregates. This means that there is an interaction between the transition dipoles which are largely displaced along one axis with a constant angle during the LB transferring process. This result suggests that the different aggregation forms in the monolayer assemblies can be obtained by the different transferring methods. For both X-type and Y-type films of TFPP's gave dichroisms at a Soret band, a well ordered molecular orientation in the films were demonstrated. The results of Ip>Is in any case show that the porphyrin molecules have a tendency to be oriented with their macrocyclic planes oblique in the films. This is consistent with the results deduced from the π-A isotherm.

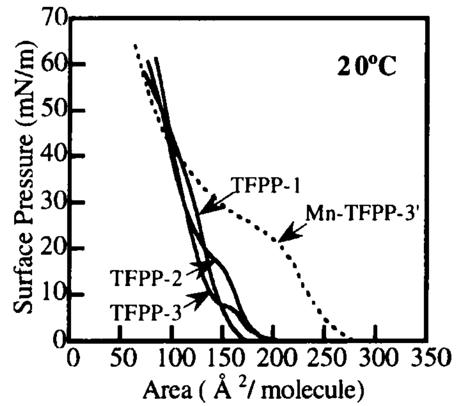


FIGURE 2 π-A isotherms of TFPP and Mn-TFPP monolayers at 20°C multilayers

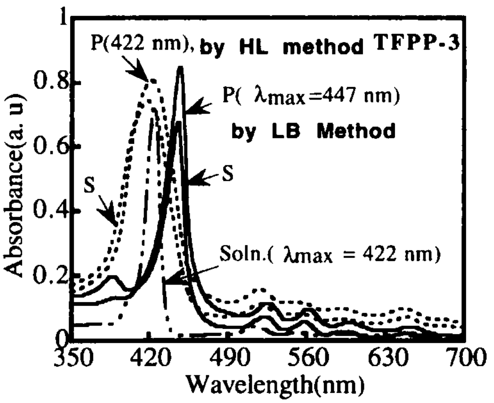


FIGURE 3 UV-vis spectra for TFPP-3 in solution and polarized UV-vis spectra in the the multilayers

The experimental results for the third-order nonlinear optical properties of the porphyrins are summarized in Table.1. The third-order nonlinear optical response $\chi^{(3)}$ of vertically transferred films(Y-type films) is remarkably different from those of the horizontally transferred films (X-type films). The former show larger $\chi^{(3)}$, about 10 times to the corresponding the later films. These results indicate that the macroscopic $\chi^{(3)}$s are larger in the red-shifted films(Y-type films) in which there is an extend π-electron system than in other films(HL method). Similar results were also observed in the phthalocyanine films.[6]

TABLE.1 The absorption maxima and $\chi^{(3)}$ values in the films of porphyrin derivatives with different transferring methods at 20 mN/m

Sample	λ_{max}(nm)	Method	Shift (nm.)	$\chi^{(3)}$ esu. (10^{-13})
TFPP-1	423	HL	+3	7.0
TFPP-1	430	LB	+10	18.0
TFPP-3	422	HL	+0	2.0
TFPP-3	447	LB	+25	26.0
Mn-TFPP-3'	478	HL	-2	4.4
Mn-TFPP-3'	480	LB	0	20.0

In conclusion, the third-order optical susceptibilities of the larger conjugated system tetraphenylporphyrin derivatives were studied by THG measurement and compared with corresponding values for X-type films. The third-order optical properties of Y-type films are enhanced with number of electrons in the extend π- system due to the electronic interactions between molecules of porphyrin which are produced by the LB deposition.

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