Second-order nonlinear optical properties of amphiphilic porphyrins in Langmuir–Blodgett monolayer assemblies

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Abstract

Optical second harmonic generation (SHG) from the Langmuir–Blodgett (LB) monolayer assemblies of amphiphilic porphyrin and its some metal complexes has been investigated. Distinct SHG responses were observed with monolayers of amphiphilic 5-(4-N-hexadecylpyridinium)-10,15,20-triphenylporphine bromide (free base: H_2 porphyrin) and its magnesium (Mg), copper (Cu), and zinc (Zn) complexes. The efficiency of SHG was in the order of Mg → Zn → Cu → H_2-porphyrins, which could be well correlated with the order of the first reduction potential of the porphyrin. The result indicated that SHG was mainly attributed to charge transfer from the porphyrin ring to the pyridinium group. The tilt angle of the molecular hyperpolarizability for the Zn porphyrin was evaluated.

Keywords: Optical second harmonic generation; Porphyrin; LB Monolayer; Charge transfer

1. Introduction

Materials with highly efficient nonlinear optical (NLO) properties are one of the most important research targets in material science. As to quadratic NLO properties, a number of organic compounds with a pair of electron-donor- and electron-acceptor sites at the end of π-conjugating system has been prepared, and the second harmonic generation (SHG) activity has been investigated [1]. A recent study revealed that porphyrins with quadratic NLO properties could be prepared by introducing donor- and acceptor groups at the meso positions of porphyrin moiety [2]. Porphyrins with pyridyl groups at the meso positions were covalently bound to oxide surface and a relatively large SHG response was attributed to the delocalized π-electrons in the porphyrin derivatives [3]. Effects of central metal ions of porphyrins on quadratic NLO properties have not been reported so far.

In the present paper, several metal complexes of amphiphilic porphyrins were prepared and SHG responses were examined. The Langmuir–Blodgett (LB) technique was used to prepare monolayer films of the amphiphilic porphyrins, since characteristics of porphyrins in LB assemblies are rather well understood [4–14]. As a consequence, the second harmonic (SH)

light intensity from the monolayer was substantially affected by the choice of central metal ions. The origin of SHG and structural property of the monolayer are discussed.
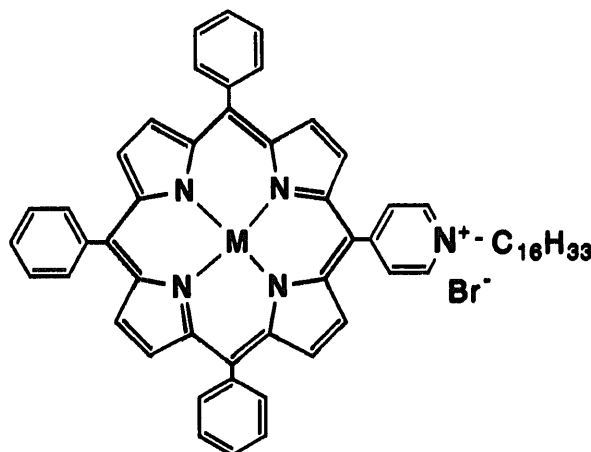
M = H₂, Mg, Cu, Zn

2. Experimental detail

An amphiphilic porphyrin, 5-(4-N-hexadecylpyridi-nium)-10,15,20-tetraphenylporphine bromide [15] (ab-

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breviated as H_2 porphyrin) and its Mg, Cu, and Zn complexes were prepared. The purity of the compound was confirmed by elemental analysis, NMR, and electronic absorption spectra. Other chemicals were used as received.

The porphyrin monolayer was formed by spreading the chloroform solution (5×10^{-4} M) onto a pure water surface. The surface pressure-molecular area (π-A) isotherm was measured with a film balance controller (USI System FSD-110) at a controlled temperature (290 K) and a compression speed of 20 mm min^{-1}. Usually, the monolayers were transferred onto both surfaces of a glass substrate by withdrawing the glass substrate from the water pool. Deposition of a monolayer on one surface of the substrate was obtained by the use of two glass substrates superimposed on each other. The glass substrate surfaces were cleaned as described previously [16].

The redox potential was evaluated from cyclic voltammogram as obtained with a YANACO P-8 Polarograph. Platinum wires (0.5 mm diameter) were used as working and counter electrodes, together with an Ag/AgCl electrode as a reference. An acetonitrile solution containing the porphyrin (5×10^{-5} M) and tetrabutylammoniumperchlorate (0.1 M) was deaerated before measurements.

Electronic absorption spectra were recorded with a Shimadzu UV-2200 spectrophotometer.

The experimental setup for SHG measurements has been described previously [16]. Briefly, p- or s-polarized laser light from a Q-switched Nd:YAG laser (1064 nm, 5-7 ns pulse duration, 20 mJ pulse energy, 5-10 Hz repetition rate) passed through the sample. Either p- or s-polarized component of the SH signal was detected by the time-gated detection equipments. As to the Mg porphyrin, which is unstable under aerobic conditions, the SHG measurements were quickly carried out just after sample preparation.

3. Results and discussion

Owing to their amphiphilic nature, the present porphyrins afforded monolayer films on a water surface. The π-A isotherms for the porphyrins are shown in Fig. 1. The isotherms for H_2-, Mg-, and Cu porphyrin indicated preservation of condensed phases without collapse up to 30 mN m^{-1}. As to the Zn porphyrin, an expanded phase was observed at lower surface pressures (<10 mN m^{-1}) in addition to a condensed phase at higher surface pressures (20-40 mN m^{-1}). The extrapolated limiting areas are summarized in Table 1.

On the basis of a CPK molecular model, the molecular plane of porphyrin skeleton including three phenyl and one pyridinium groups is estimated to cover about 2 nm^2. A quite similar value (1.96 ± 0.15 nm^2) for the
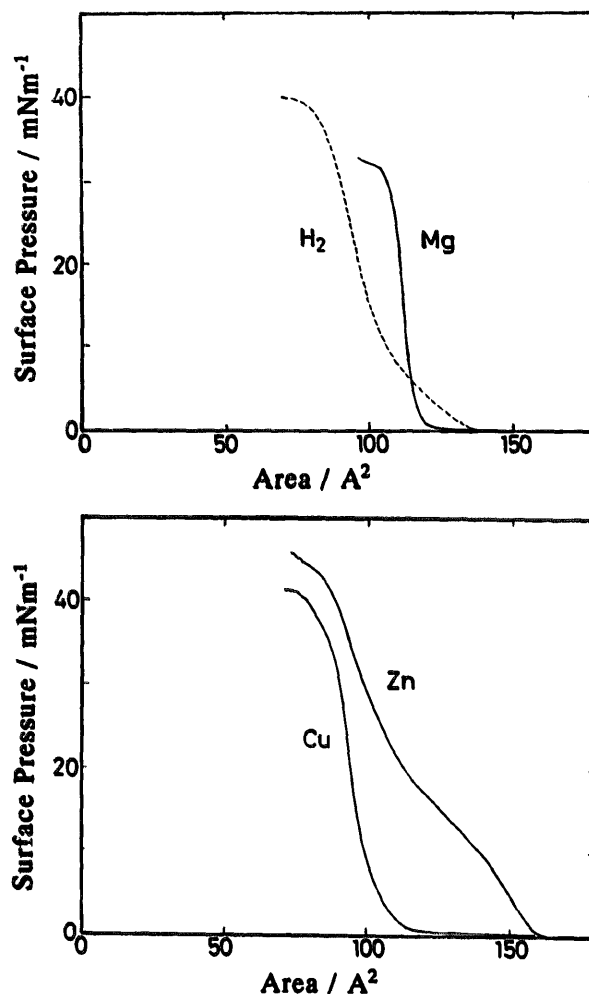

Fig. 1. Surface pressure-area isotherms of porphyrins at 290 K: free base (H_2), magnesium (Mg), copper (Cu), and zinc (Zn) porphyrin.

Table 1
Molecular area as evaluated from π-A isotherm

Compound	Molecular area (nm^2)	
H_2 porphyrin		1.20
	1.96 ± 0.15, 0.92 ± 0.12 [a]	
Mg porphyrin		1.10
Cu porphyrin		1.05
Zn porphyrin	1.60 [b]	1.25

[a] Obtained from the LB multilayers of the mixture of free base porphyrin and arachidic acid at 291 K [9].
[b] Liquid-expanded phase.

porphyrin moiety had been obtained with the Y-type LB multilayer film of the mixture of H_2 porphyrin and arachidic acid at surface pressures less than 30 mN m^{-1}, which was taken to indicate parallel alignment of the porphyrin ring with respect to water surface [9]. The molecular areas of the condensed phases (1.05-1.30 nm^2) are roughly half that of the estimated molecular area (2 nm^2), and partial stacking of the porphyrin rings was suggested.

The electronic absorption spectra of monolayer assemblies of the porphyrins deposited at 25 mN m^{-1} and the corresponding spectra in acetonitrile are shown in Fig. 2. The monolayer sample of each porphyrin exhibited distinct red shift (10–15 nm) and considerable broadening of the Soret band as compared with that in an acetonitrile solution. Slight red shifts of the Q bands were also observed. These spectral features (red shift and broadening) are typical for porphyrin aggregates [6–8,14,15].

Four meso positions of the present porphyrin are occupied by one pyridinium group and three phenyl groups, so that it must possess a second-order molecular hyperpolarizability β. In fact, the monolayer assembly of the present porphyrin generated the distinct SH signal as typically shown in Fig. 3 for the Zn porphyrin deposited at 25 mN m^{-1}. The monolayer sample on both substrate surfaces showed clear interference fringe patterns arising from dephasing of SH signals at front and rear surfaces (Fig. 3(a)). The SH signal became substantially smaller in the case of the monolayer sample on one substrate surface (Fig. 3(b)). Interference fringe patterns still remained slightly, probably because of the
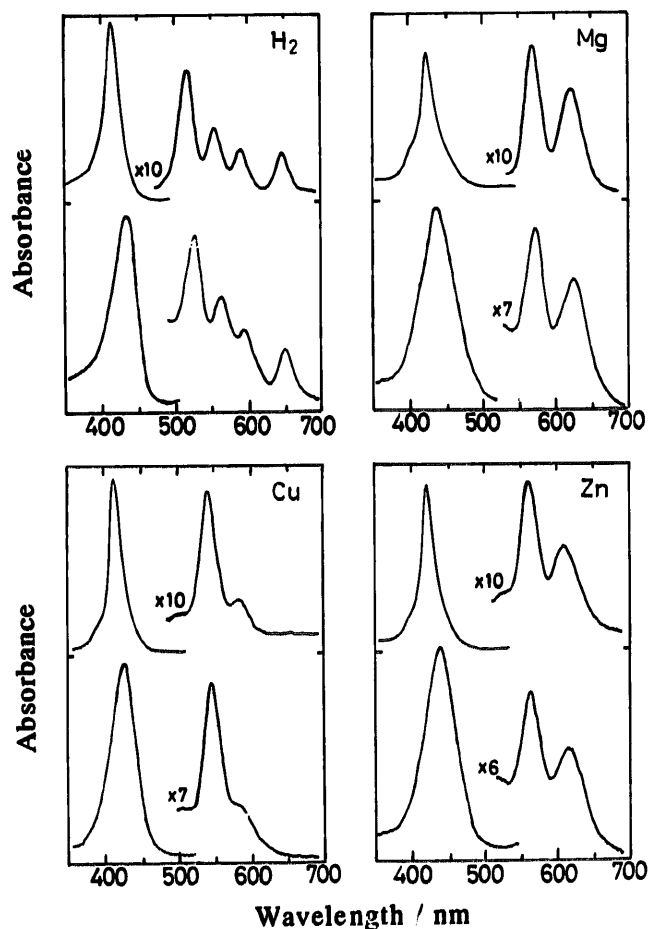

Fig. 2. Absorption spectra of porphyrins in acetonitrile (top) and the corresponding LB monolayer assemblies deposited at 25 mN m^{-1} (bottom).
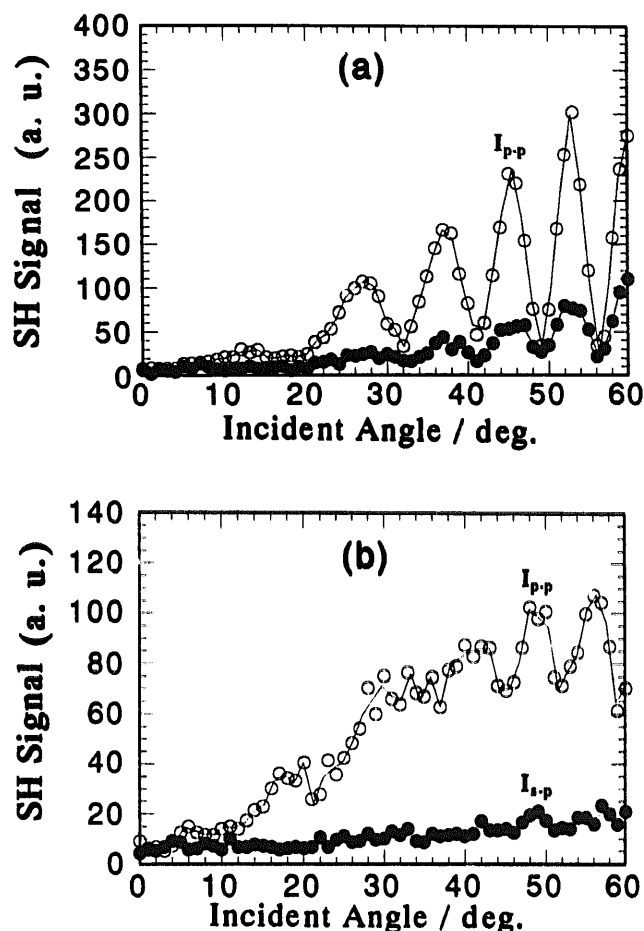

Fig. 3. Angular dependence of the transmitted SH signals from the Zn porphyrin monolayer assembly deposited at 25 mN m^{-1} on both surfaces (a) and one surface (b) of the substrate. The incident laser beam was p- or s-polarized, and p-polarized SH signals are denoted by $I_{p\text{-}p}$ and $I_{s\text{-}p}$, respectively.

interference with the SH signal from the glass surface. The SH signal intensity at an incident angle of 45° was estimated by interpolating the values at fringe maxima (Fig. 3(a)), unless otherwise noted. As shown in Fig. 4, the SH signal intensity at 45° incident angle could be well correlated with the first reduction potential ($E_{1/2}^{red}$) of the porphyrin ring. The $E_{1/2}^{red}$-value shifted to the cathodic direction with increasing the electron-donating property of the central metal ion. Since the pyridinium group is electron-accepting, these results suggest that the SHG under discussion is mainly ascribed to the electric polarization due to intramolecular charge-transfer from the porphyrin moiety to the pyridinium group; the axis of the molecular hyperpolarizability must coincide with C$_2$-axis of the porphyrin moiety.

The π–A isotherm of the Zn porphyrin indicated development of two different phases with surface compression. There was no appreciable difference in the shape of absorption spectra between monolayer films deposited at the two different phases (<10 and 20–40 mN m^{-1}). The absorbance at 438 nm, however,
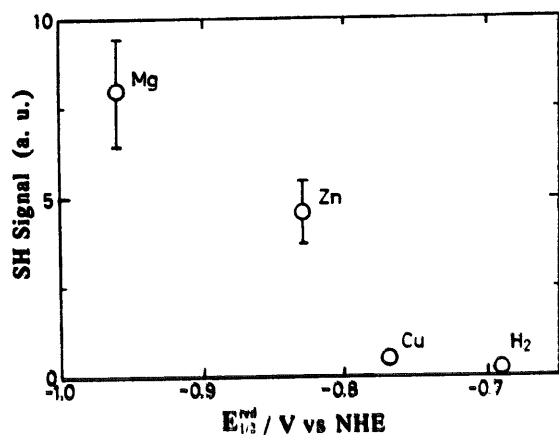
Fig. 4. Relationship between the SH signal intensity at the incident angle of 45° and the first reduction potential of the porphyrin ($E_{1/2}^{red}$/V vs. NHE).
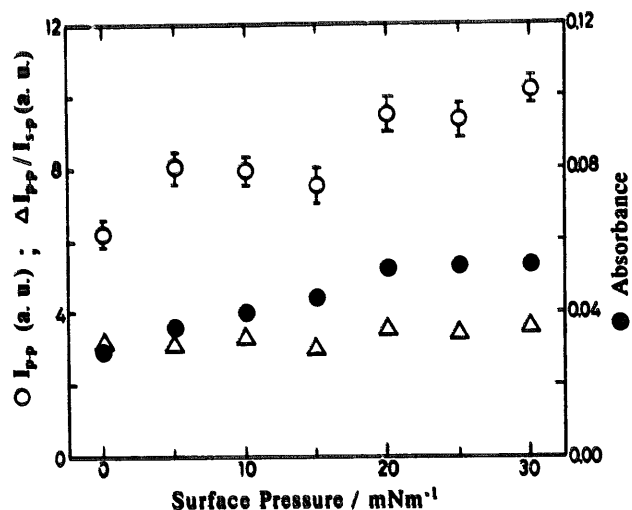

Fig. 5. Relationships between the SH signal and the absorbance (438 nm) of the Zn-porphyrin monolayer assembly as prepared at several deposition pressures: O, I_{p-p}; Δ, I_{p-p}/I_{s-p}; and ●, absorbance at 438 nm.

increased by ca. 40% on going from 10–30 mN m^{-1} in the surface pressure of film deposition (Fig. 5). The SH signal intensity of the Zn porphyrin monolayer also increased in accordance with the absorbance at 438 nm. While, the polarization ratio of the p-p and s-p SH signal intensities, I_{p-p}/I_{s-p}, which should reflect the average tilt angle of the molecular hyperpolarizability [17], was almost independent of the deposition pressure. Thus, the orientation of porphyrin moiety with respect to the film surface must be almost alike between the two phases. These results clearly indicate that the good correlation between the absorbance and the SH signal intensity is ascribed to increase in the porphyrin density with the deposition pressure, and not to orientational change in the porphyrin.

Since the s-polarized SH signals (I_{p-s} and I_{s-s}) were negligibly small, one can assume $C_{\infty v}$ for the point symmetry of the LB monolayer assembly [17]. Under
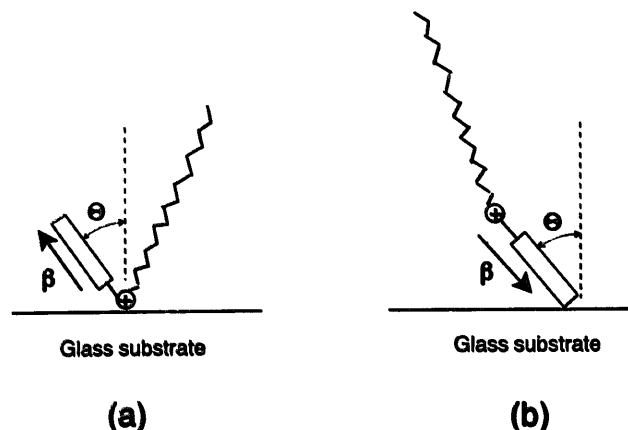

Fig. 6. Possible structures for the porphyrin LB monolayer assembly. The porphyrin ring is denoted by □, and the pyridinium ring by ⊕. The average tilt angle of the molecular hyperpolarizability (β) is defined as Θ.

the projection model, the average tilt angle (Θ) of the axis of hyperpolarizability (β), which coincides with molecular axis in the present case, can be estimated from the ratio of polarized SH signal intensities:

$$I_{p-p}/I_{s-p} = 1/4(3 + \chi_{\parallel}/\chi_{\perp})^2$$

$$\Theta = \tan^{-1}(2\chi_{\perp}/\chi_{\parallel})^{1/2}$$

where I_{p-p} and I_{s-p} are transmitted SH signals at an incident angle of 45°, and second-order nonlinear susceptibility tensor components parallel and perpendicular to the symmetry axis (surface normal) are denoted by $\chi_{\parallel}$ and $\chi_{\perp}$, respectively [17]. The Mg and Zn porphyrin monolayer assemblies deposited on the front surface of the substrate at 25 mN m^{-1} showed comparable Θ-values (43°–50°). The SH signal intensity of the Cu and H_2 porphyrins were too small to be used for evaluating reliable values.

Two alternative cases with opposite orientations of polarization axis (β) should be considered (Fig. 6). The case (a) must be favourable in terms of the electrostatic interaction between the pyridinium group and the glass surface. As to case (b), a similar situation has been reported for 5-(N-tetradecyl-4-pyridino)-10,15,20-tri-p-tolylpoyphyrin, whose structure is very close to our H_2 porphyrin, at an air–water interface under surface pressures of less than 30 mN m^{-1} [14]. An example of case (a) orientation has been reported on H_2 porphyrin in Y-type LB multilayer on the basis of polarized absorption measurements [9]. Several attempts are under progress to differentiate between the above alternative orientations.

4. Conclusions

The amphiphilic porphyrin and its metal complexes exhibited SHG in the LB monolayer assemblies. The

SHG and electrochemical studies indicated that the second-order NLO response of the present porphyrin was ascribed mainly to the electric polarization between the pyridinium group and the porphyrin ring. The choice of central metal ion was apparently useful to modify molecular hyperpolarizability of the present porphyrins. Also, construction of highly ordered molecular assembly at monomolecular levels is an important key to practical applications of LB films as SHG materials.

Acknowledgments

References

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