

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

TITLE SYNTHESIS AND CHARACTERIZATION OF A COVALENTLY BOUND
SELF-ASSEMBLED MACROCYCLE MONOLAYER THIN FILM FOR NONLINEAR
OPTICAL MATERIALS

AUTHOR(S) DeQuan Li, Basil Swanson, Jeanne Robinson, and Mark A. Hoffbauer

SUBMITTED TO SPIE Proceedings, Conference on Nonlinear Optics, Los Angeles,
CA, January 20-22, 1992

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce
the published form of this contribution or to allow others to do so for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed in the auspices of the U.S. Department of Energy.

MASTER

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545



Synthesis and characterization of a covalently bound self-assembled macrocycle monolayer thin film for nonlinear optical materials

DeQuan Li and Basil I. Swanson
Isotope and Nuclear Chemistry Division
and
Jeanne M. Robinson and Mark A. Hoffbauer
Chemical and Laser Sciences Division

Los Alamos National Laboratory, Los Alamos, NM 87545

ABSTRACT

Synthesis and characterization of covalently bound self-assembled 5,10,15,20-Tetra(4-pyridyl)-21H,23H-porphine (TPyP) monolayer superlattices on various oxide surfaces such as fused silica, glass or silicon are described. The mono-molecular thin film structures are characterized by UV-visible ($\lambda_{\text{max}} = 447 \text{ nm}$) and FTIR-ATR spectroscopy. In addition, X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS) studies are used to confirm the formation of a self-assembled monolayer on the fused-silica surface. Attractive features in these complexes are their second-order nonlinear optical properties, enhanced by the completely delocalized π -electrons. Second harmonic generation measurements have been used to determine the uniformity of the film, the relative and absolute magnitudes of nonzero elements of the nonlinear susceptibility, $\chi^{(2)}$, and the average molecular orientation of the chromophores.

1. INTRODUCTION

Highly ordered molecular assemblies in solids can lead to materials with extremely interesting properties such as nonlinear optical phenomena, isotropic conduction, and permanent magnetism. The general synthetic strategy of polar dye multilayer nonlinear optical materials was developed by Li and coworkers^{1,2,3} and more recently employed by others.⁴ The strategy consists of deposition of a coupling layer, which in turn can anchor a chromophore/dye possessing large nonlinear susceptibilities. The nonlinearities of these films can be comparable or greater than those of LiNbO_3 , which is one of the highest $\chi^{(2)}$ inorganic materials currently being used.

Theoretical and experimental studies reveal that the first order nonlinear optical susceptibilities can be tremendously enhanced by both intramolecular charge transfer and large absorption coefficients.⁵ Organic chromophores have recently attracted attention⁶⁻⁹ due to their intense optical absorptions and the possibility of attaching donor and acceptor ligands to the dye skeleton. We report here a nonlinear optical thin film material based on a covalently bound self-assembled 5,10,15,20-Tetra(4-pyridyl)-21H,23H-porphine (TPyP) monolayer superlattice in which intramolecular charge transfer is not significant but optical absorptions are quite strong.

2. CONSTRUCTION OF PORPHINE MONOLAYER

Fused silica and silicon substrates were treated by ultra-sonic cleaning in a 10% detergent solution for 10 minutes. The silica substrates were then boiled in 1% ethylenediaminetetraacetic acid, tetrasodium salt (Na₄EDTA) for 10 minutes followed by a 10 minute ultra-sonic treatment in 1% Na₄EDTA at ambient temperature. Both substrates were then cleaned by exposure to argon plasma for approximately 30 minutes at a pressure of about 0.5 torr.

The general strategy we have employed for synthesizing the self-assembled monolayers is illustrated in Figure 1. The cleaned substrates were dipped into either *p*-(chloromethyl)phenyltrichlorosilane or *p*-(iodomethyl)phenyltriiodosilane for 24 hours for the growth of a coupling layer as illustrated by step (a) in Figure 1. The coupling layer is bound to the surface oxide (SiO₂) via a siloxane linkage which should provide high chemical and structural stability in addition to structural regularity, as controlled by the density of surface hydroxyl groups. Either the chloro or iodo functional groups are active enough to be used to anchor a chromophore/dye molecule to the coupling layer at a properly selected elevated temperature. A monolayer of the 5,10,15,20-Tetra(4-pyridyl)-21H,23H-porphine superlattice was covalently attached to the coupling layer as illustrated by step (b) in Figure 1 by refluxing the coupling layers in 1.5 mM ethanol/chloroform (1:9) solution of TPyP for 2 days at 90 °C. The porphine monolayer absorbs slightly in the UV-visible region. Its maximum absorption occurs at 447 nm with 0.0295 absorbance. No differences in the absorption spectra were observed between self-assembled porphine monolayer films using either Cl⁻ or I⁻ counter ions to grow the thin films. No detectable changes were observed in the UV-visible absorption spectra for covalently bound self-assembled porphine macrocycles stored in air at ambient temperatures for one month.

Insert figure 1 here

Figure 1. Synthetic scheme to form a covalently bound self-assembled monolayer of 5,10,15,20-Tetra(4-pyridyl)-21H,23H-porphine. The reaction conditions were as follows : (a) dry chloroform at 25 °C; (b) chloroform/ethanol (9:1 by volume) at 90°C

3. STRUCTURAL CHARACTERIZATION

The formation of monolayer thin films of *p*-(chloromethyl)phenyltrichlorosilane or *p*-(iodomethyl)phenyltriiodosilane can be conveniently monitored by the changes in the water contact angle, which is less than 5 degrees for a freshly cleaned substrate and is approximately 50 degrees following the deposition of the organic monolayer. Covalent bonding of this organic coupling monolayer can also be confirmed by UV absorption spectroscopy. Aromatic phenyl absorptions at 195 nm were observed by growing these thin films on fused silica surfaces. After anchoring the porphine macrocycle, a characteristic change in its intense absorption from 412 nm to 447 nm occurs in the UV-vis spectroscopy which suggests the quaternization of the pyridyl group. In aqueous solution, a model compound 5,10,15,20-tetrakis(1-methyl-4-pyridyl)-21H, 23H-porphine (tetra-*p*-tosylate salt) has an absorption at 422 nm with an extinction coefficient, ϵ , of $1.5 \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}$. Thus, the estimated surface density of the porphine macrocycle should be $\sim 2 \times 10^{-7} \text{ mmol/cm}^2$ or ~ 1.2 porphine macrocycle per 100 \AA^2 . This corresponds roughly to the dimensions of the actual porphine molecules.

FTIR spectroscopy of these monolayer films was performed on a Bio-Rad FTS-40 with a Harrick Seagull variable-angle reflection attachment in both *p* and *s* polarized geometry. Infrared studies on these porphine macrocycle monolayers can be conveniently performed by growing these films on polished Si wafers which are transparent from 4000 cm^{-1} to 1500 cm^{-1} . The functionalized Si wafers were then pressed against a ZnSe hemispherical crystal with a miniature pressure device to assure optical contact. A single attenuated total reflection from the interface of ZnSe crystal and Si/porphine monolayer was collected with 1024 scans and 8 cm^{-1} resolution. Further details of the experimental setup will be discussed elsewhere.¹⁰ Two CH_2 vibration bands were observed at 2929 cm^{-1} and 2854 cm^{-1} which correspond to symmetric, $\nu_s(\text{CH}_2)$, and asymmetric, $\nu_a(\text{CH}_2)$ stretching vibrations, respectively. In addition, two strong vibrations were observed at 1635 cm^{-1} and 1593 cm^{-1} which represent the aromatic ring vibrations from C=C or C=N stretches. The intensities of these vibrations of the aromatic rings in the *p*-polarized geometry are about twice as strong as those in the *s*-polarized geometry, indicating relatively low anisotropy. **This implies that round, disk-like structures exist on the surface oriented along the surface normal with no preferred azimuthal orientation. However, these monolayers do possess highly ordered structures along the surface normal.**

X-ray photoelectron spectroscopic (XPS) measurements of these porphine macrocycle monolayer films indicate the presence of the elements C(1s), N(1s), O(1s), Si(2s and 2p), and Cl(2p) or I(3d). The intensities and relative attenuations of the substrate elements (Si and O) suggest that the thickness of organic films is on the order of a monolayer. Secondary ion mass spectroscopy (SIMS) measurements were also performed on these molecular assemblies. In addition to confirming the individual elements present on the surface, porphine fragments were observed at mass $m = 90-100$. The details of both the XPS and SIMS experiments will be discussed elsewhere.¹⁰

4. NONLINEAR OPTICAL PROPERTIES

The nonlinear optical properties of the monolayer films were investigated using second harmonic generation (SHG) in a transmission geometry. The SHG measurements were made using the 1064 nm light from a 30 Hz Nd:YAG regenerative amplifier system that provided pulses with ~ 100 psec temporal width and energies at the thin film surface of up to **1 mJ**. The incident laser polarization could be varied to

select either *p*- or *s*-input, and was mildly focused onto the surface (spot size ~1 mm in diameter). The transmitted SHG signal at 532 nm was separated from the fundamental beam using a combination of dichroic mirrors and color filters, passed through a polarizer that could be rotated to select either the *p*- or *s*-polarized component, and detected using a cooled photomultiplier tube. A computer controlled gated boxcar integrator was used to measure the transmitted second harmonic light. The computer also controlled the rotation of the substrate within the plane of incidence. The SH signal was detected as the substrate was rotated from normal incidence (0°) to grazing incidence ($\sim 90^\circ$).

No strong azimuthal orientation dependence was observed within the plane of the self-assemblies in the SHG experiments, a result which was also supported by the lack of anisotropy in the FTIR measurements. These results indicate that the films possess uniaxial symmetry about the surface normal.¹ Only two independent tensor elements of $\chi^{(2)}$ are then nonvanishing, χ_{zzz} and $\chi_{zxx}=\chi_{zyy}$.

The transmitted *p*-polarized SH intensity measured for a *p*-polarized incident beam, $I_{p,p}(2\omega)$, is shown in Figure 2 as a function of the incident angle. The two major features observed are the broad envelope of the SHG intensity as a function of incident angle, and the pronounced interference pattern

Insert Figure 2 here

Figure 2. Transmitted *p*-polarized SH intensity at 532 nm as a function of the angle of the *p*-polarized incident beam with respect to the surface normal for a fused quartz substrate which was functionalized with porphine self-assembled macrocycle complexes on both sides. The data points are connected with a solid line for visual clarity. The solid line describing the broad envelope is a theoretical fit using the model discussed in the text.

within the envelope. The interference fringes of the SH intensity arise from the interaction of the second harmonic waves from the self-assembled films on either side of the silica surfaces. Their complete destructive interference, i.e. the zero minima, indicates that the thin films on both sides of the substrate are essentially identical, possessing the same molecular orientation or polar angle, number density, chemical structure and thickness.

According to the theoretical model described by Bloembergen¹¹ and Wong,¹² the SHG angular dependent envelope is determined by the ratio of the second-order nonlinear susceptibility tensor elements χ_{zzz}/χ_{zxx} , and refractive indices, n , of the films and substrate. Using refractive indices of $n_{\text{air}}(\omega) = 1.00$, $n_{\text{glass}}(\omega) = 1.50$, and $n_{\text{glass}}(2\omega) = 1.55$, we obtain the dispersion of the refractive index of film, $n_{\text{film}}(\omega)/n_{\text{film}}(2\omega) = 1.2$. The solid line shown in Figure 2 shows the fit to the envelope of the experimental data using this ratio in the theoretical model. This result has several important implications. First, the dispersion of the refractive index is approximately one, indicating that the experiments were performed under nonresonant conditions, in agreement with the lack of features in the UV-visible spectra at 2ω . Secondly, the refractive index ratio suggests that the assumption of minimal dispersion within the theoretical model is reasonable for these films.

Assuming typical values of the refractive index for organic films of $n_{\text{film}}(\omega) = 1.60$ and $n_{\text{film}}(2\omega) = 1.65$, a ratio of $\chi_{zzz}/\chi_{zxx} = 1.8$ was extracted from the fit with $n_{\text{film}}(\omega)/n_{\text{film}}(2\omega) = 1.2$ (Figure 2). The measured ratio χ_{zzz}/χ_{zxx} can be used to determine the average molecular orientation angle, $\langle\psi\rangle$, of the chromophore with respect to the surface normal. For aromatic molecules with delocalized electrons, the molecular tensor along the dipole direction, β_{zzz} , typically predominates. (Shen in Hall's book) The in plane (z-x) transition dipole moments are often larger than those perpendicular to the molecular plane and transition moments along z are larger than those along x. Assuming that β_{zzz} is the dominant tensor, Equation (1) and Equation (2) relate the magnitude of the nonvanishing nonlinear susceptibilities of the film to $\langle\psi\rangle$.

$$\chi_{zzz} = NC \beta_{zzz} \langle \cos^3 \psi \rangle \quad (1)$$

$$\chi_{zxx} = \frac{1}{2} NC \beta_{zzz} \langle \sin^2 \psi \cos \psi \rangle \quad (2)$$

N is the molecular number density and C is the local field correction factor. The ratio of these two equations yields $\chi_{zzz}/\chi_{zxx} = 2\langle \cot^2 \psi \rangle$. For $\chi_{zzz}/\chi_{zxx} = 1.8$ obtained from the fit to the SH envelope in Figure 2, the average angle between the molecular dipole moment and the surface normal, $\langle\psi\rangle = 48 \pm 10^\circ$, was determined for these porphine self-assembled monolayers. The uncertainty in this angle is estimated from the refractive index dispersion, which is $\sim 20\%$ higher than its theoretical value.

Theoretical monolayer thickness of 23.4 \AA was estimated by using crystallographic porphine bond length and bond angles¹³ for chromophore layer and standard bond distance¹⁴ for the coupling layer. Calibrating the observed SHG intensity to that observed for a z-cut quartz substrate **REF**, a value of $\chi_{zzz} = 1.5 \times 10^{-8} \text{ esu}$ can be obtained for a monolayer film with a thickness of $\sim 15.7 \text{ \AA}$ employing the theoretical molecular dimension of $\sim 23.4 \text{ \AA}$ and an average polar angle of $\langle\psi\rangle$ of ~ 48 degrees. This value for χ_{zzz} compares favorably with other self-assembled monolayer thin films of 4-[N,N-bis(3-hydroxypropyl)amino]styryl-4'-pyridine and 4-[4-[N,N-bis(2-hydroxyethyl)amino]phenylphosphonic acid in the literature. The χ_{zzz} is about an order of magnitude smaller than the former¹ and about the same as the later.⁴ This result indicates that intramolecular charge transfer can affect $\chi_{zzz}^{(2)}$ in the degree of one to two order of magnitude in general organic system. By incorporating charge transfer functionalities in the present system the $\chi_{zzz}^{(2)}$ value can further increased.

Some comments on these $\chi^{(2)}$ values.

5. CONCLUSIONS

The results presented in this paper show that SHG can be a very useful technique for the characterization of self-assembled monolayer thin film systems. The observation of a relatively large SHG response in the porphine macrocycle monolayer films can be attributed to the completely delocalized π -electrons in the porphine derivatives. The average molecular orientation of the complexes relative to the substrate has also been experimentally determined. Since strong optical absorptions can be extremely important in terms of enhancing nonlinear optical susceptibilities, future experiments using resonantly enhanced SHG will be important in understanding these covalently bound self-assembled macrocycle monolayer systems.¹⁰

6. REFERENCES

1. D. Li, M. A. Ratner, T. J. Marks, C. Zhang, J. Yang, G. K. Wang, *J. Am. Chem. Soc.* vol. 112, pp. 7389, 1990.
2. D. Li, T. J. Marks, C. Zhang, J. Yang, G. K. Wang, *SPIE* vol. 1337, pp. 341, 1990.
3. D. Li, T. J. Marks, T. Zhang, G. K. Wang, *Synthetic Metals* vol. 41-43, pp. 3157, 1991.
4. H. E. Katz, G. Scheller, T. M. Putvinski, M. L. Schilling, W. L. Wilson, C. E. D. Chidsey, *Science* vol. 254, pp. 1485, 1991.
5. D. Li, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* vol. 110, pp. 1707-1715, 1988.
6. G. Khanrarian, "Nonlinear Optical Properties of Organic Materials II," *SPIE Proc.* vol. 1147, 1990.
7. J. Messier, F. Kajar, P. Prasad, D. Ulrich, Eds.; "Nonlinear Optical Effects in Organic Polymers," Kluwer Academic Publishers: Dordrecht, 1989.
8. A. J. Heeger, J. Orenstein, D. R. Ulrich, Eds. "Nonlinear Optical Properties of Polymers," *Mats. Res. Soc. Symp. Proc.* vol. 109, 1988.
9. D. J. Williams, *Angew. Chem., Int. Ed. Engl.* vol. 23, 690, 1984.
10. D. Li, B. I. Swanson, J. M. Robinson, and M. A. Hoffbauer, manuscript in preparation.
11. N. Bloembergen and P. S. Pershan, vol. 128, pp. 606-622, 1962.
12. T. Zhang, C. Zhang, G. K. Wong, *J. Opt. Soc. Am. B.* vol. 7, pp. 902, 1990.
13. K. M. Smith, "Comprehensive Heterocyclic Chemistry," pp. 386, Pergamon Press, New York, 1984.
14. David R. Lide, "Handbook of Chemistry and Physics, 72nd Ed.", pp. 9-2-9-17, CRC Press, Boston, 1991.



