

## Porphyrins as Second Order Nonlinear Optical Materials

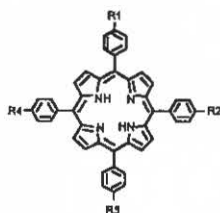
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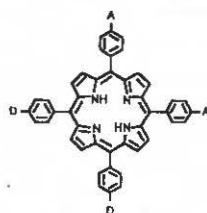
Molecules with nonlinear optical (NLO) properties have been extensively investigated due to their potential applications for high-speed optical communication and high density data storage [1-5]. Porphyrins have traditionally provided a versatile synthetic base from which to design molecules with specific physical and chemical properties. Their large extended  $\pi$ -system and structural stability makes them exceptional candidates for the study of their NLO properties. Previous work has shown that porphyrins can be successfully tailored to exhibit substantial *molecular* second order NLO response as given by  $\beta$ , the first *molecular* hyperpolarizability coefficient [6]. The goal of this project was to take these molecules with high  $\beta$  values and assemble them into a material with a high second order NLO response as given by  $\chi^{(2)}$ , the second order nonlinear optical susceptibility, and consequently investigate the feasibility of porphyrins assemblies as a  $\chi^{(2)}$  material for device applications.

Three classes of porphyrins were chosen for this study and were based on two factors: dipole strength of the donor-acceptor pair and the number of easily polarizable electrons.

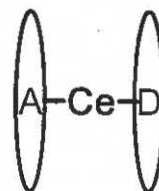


Class I

(Amino-Nitro substituted)



Class II

*(cis-2 derivatives)*

Class III

(Ce *bis*-porphyrin)

**Class I** explores the effects of the *number* of donor-acceptor groups [Porphyrins studied:  $H_2(an_3P)$ ,  $H_2(cis-a_2n_2P)$ ,  $H_2(a_3nP)$ ,  $H_2(a_4P)$  where  $a$  = 4-aminophenyl, 4-(N-octadecylamido)phenyl, or 4-(N-octadecylamino)phenyl;  $n$  = 4-nitrophenyl;  $P$  = 5,10,15,20 substituted porphyrin]. **Class II** examines the effect of varying the *strength* of *cis*-substituted donor-acceptor pairs [Porphyrins studied:  $H_2(cis-a_2n_2P)$  and  $H_2(cis-h_2py_2P)$  where  $h$  = 4-hydroxyphenyl or 4-methoxyphenyl and  $py$  = 4-pyridyl or 4-(N-octadecyl)pyridiniumyl]. **Class III** looks at the effects of cofacial porphyrins [where (A) is the acceptor ring, tetra(4-pyridyl)porphyrinate(2-) or tetra(4-(N-octadecyl)pyridiniumyl)porphyrinate(2-) and (D) is the donor ring, tetra(4-methoxy)phenylporphyrinate(2-)].

In order to create a molecular assembly for a high  $\chi^{(2)}$  material, the molecules must be in a noncentrosymmetric arrangement. Otherwise, the second order NLO response generated from one molecule will be cancelled by another molecule which has inverse symmetry to the first molecule in the assembly. Also, since  $\chi^{(2)}$  is a tensor, the exact orientation of the molecules in the media must be ascertained to assess its viability as a material for optical devices [7].

The first task was to determine which alignment technique would best give a noncentrosymmetric arrangement of molecules. Of all the possible alignment techniques available (growth of noncentrosymmetric crystals, poled polymers, and Langmuir-Blodgett films), the

Langmuir-Blodgett (LB) technique has proven to orient molecules with the largest degree of chromophore alignment and chromophore density [8].

In order adapt our NLO porphyrins for use in the LB technique, the molecules must act as surfactants [9] (*i.e.* it must possess both strongly hydrophobic as well as strongly hydrophilic groups). As a result, hydrophobic chains (cholesterol and long n-alkyl chains) were attached to the porphyrin peripheries. [Porphyrins studied: 1-AMD [ $H_2(a_{n3}P)$ ], c2-AMD [ $H_2(cis-a_{2n2}P)$ ], 3-AMD [ $H_2(a_{3n}P)$ ], 4-AMD [ $H_2(a_4P)$ ], c2-AMNE [ $H_2(cis-am_{2n2}P)$ ], c2-CHOL [ $H_2(cis-c_{2p2}P)$ ], c2-PYR [ $H_2(cis-h_2Py_2P)$ ], and  $[Ce^{IV}(TPyP)(TMeP)]^{4+}I_4$  [where a = 4-octadecylamidophenyl; am = 4-octadecylaminophenyl; c = 4-(2-cholesteryloxy)ethoxyphenyl; p = 4-pyridyl; Py = 4-(N-octadecyl)pyridiniumyl; and Me = 4-methoxyphenyl]. Porphyrin films were successfully engineered and were characterized by their pressure-area isotherms and UV-visible linear dichroism (LD). The isotherm data provided a measure of the chromophore density in the film. LD was used to determine the orientation of the porphyrin planes with respect of the surface.

Porphyrin	Mma ( $\text{\AA}^2$ )	$\theta$	$\phi$	$\chi_{1064}^{(2)}$	$\chi_{1906}^{(2)}$
<b>Class I</b>				( $\times 10^{-9}$ esu)	( $\times 10^{-8}$ esu)
1-AMD	80.	32°	45°	40.	< DL
c2-AMD	110.	31°	45°	130.	2.6
3-AMD	150.	30°	45°	90.	< DL
4-AMD	225.	36°	45°	---	---
<b>Class II</b>					
c2-AMD	110.	31°	45°	130.	2.6
c2-AMNE	110.	33°	45°	120.	2.4
c2-CHOL	100.	35° <sup>a</sup>	45°	50.	< DL
c2-PYR	140.	33°	45°	100.	< DL
<b>Class III</b>					
$[Ce^{IV}(T(\pi-C18)PyP)(TMeP)]^{4+}I_4$	270.	33°	45°	40.	< DL
(Error)	( $\pm 10$ )	( $\pm 5$ )	( $\pm 5$ )	( $\pm 30\%$ )	( $\pm 30\%$ )

All NLO measurements were referenced to quartz. The detection limit (DL) @ 1906 nm was  $1.9 \times 10^{-8}$  esu.

Based on these measurements, the porphyrin films possess  $C_{\infty v}$  symmetry with the highest axis of rotation being normal to the film. This is evident from the measured azimuthal angle,  $\phi$ . In addition, all the porphyrin planes adopt a tilt angle,  $\theta$ , of about 33° with respect to the surface. The fact that all the porphyrins adopt the same orientation in LB films suggest that the interporphyrin  $\pi$ - $\pi$  interactions dominate the porphyrin alignment. This is confirmed by shifts in the UV-visible spectra of the porphyrin films [10].

The  $\chi^{(2)}$  response of the films was measured by the efficiency with which the frequency of the incident radiation can be converted into its second harmonic signal as referenced to a standard ( $\alpha$ -quartz) [11]. Initial measurements taken with incident radiation of  $\lambda=1064$  nm showed that the porphyrin films exhibit substantial  $\chi^{(2)}$  response. However, when the incident radiation was changed to  $\lambda=1906$  nm, the  $\chi^{(2)}$  responses decreased by greater than one order of magnitude. The cause of this decrease can be attributable to a resonance-enhancement of the  $\chi^{(2)}$  response @ 1064 nm.

Finally, comparing the  $\chi^{(2)}$  response of these porphyrin films with other inorganic and organic  $\chi^{(2)}$  materials illustrates one limitation with porphyrin NLO materials. Although on a per molecule basis NLO porphyrins exhibit very high  $\beta$  values (molecular) when compared to other organic / inorganic compounds, because of their size, the porphyrin LB film assemblies behave as average  $\chi^{(2)}$  materials [12]. On the other hand, the high thermal and chemical stability of porphyrin still potentially offer comparative advantages over polyene-based organic NLO materials.

#### References:

1. Eternad, S., Ed. *Nonlinear Optical Properties of Advanced Materials. Proc. SPIE-Int. Soc. Opt. Eng.* 1993.
2. *Polymer Preprints*. American Chemical Society, 1994, 35, Vol. 2.
3. Garito, A. F.; Jen, A. K.-Y.; Lee, C. Y.-C.; Dalton, L. R. in *Electrical, Optical, and Magnetic Integrated Optics*; Hornak, L. A., ed.; Marcel Decker, Inc: New York, 1993.
4. (a) *Chem. Rev.* 1994, 94.  
(b) Long, N. *Angew. Chem., Int. Ed. Engl.* 1995, 34, 21.
5. Lytel, R.; Lipscomb, G. F.; Kenney, J. T.; Binkley, E. S. in *Polymers for Lightwave and Integrated Optics*; Hornak, L. A., ed.; Marcel Decker, Inc.: New York, 1992.
6. Suslick, K. S.; Chen, C.-T.; Meredith, G. R.; Cheng, L.-T. *J. Am. Chem. Soc.* 1992, 114, 6928.
7. Boyd, R.W. *Nonlinear Optics*; Academic Press, Inc.: San Diego, 1992, p 1-32.
8. Fuchs, H.; Ohst, H.; Prass, W. *Adv. Mater.* 1991, 3, 10.
9. (a) Gaines Jr., G.L. *Insoluble Monolayers at Liquid Gas Interfaces*; Interscience: New York, 1966.  
(b) Roberts, G., Ed., *Langmuir-Blodgett Films*; Plenum Press: New York, 1990.  
(c) Ulman, A. *An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-Assembly*; Academic Press: San Diego, 1991.
10. Chou, H.; Chen, C.-T.; Stork, K. F.; Bohn, P. W.; Suslick, K.S. *J. Phys. Chem.* 1994, 98, 383.
11. Jephagnon, J.; Kurtz, S. K. *J. Appl. Phys.* 1970, 41, 1667.
12. Based on crystal structure data:  
(a) tetraphenylporphyrins (Sliver, S. J.; Tulinsky, A. *J. Am. Chem. Soc.* 1967, 89, 3331).  
(b) BaTiO<sub>3</sub> (Frazer, B. C.; Danner, H. R.; Pepinsk, R. *Phys. Rev.* 1955, 100, 745).  
(c) LiNbO<sub>3</sub> (Megaw, H. D. *Acta. Cryst., Sec. A.* 1968, 24, 583).  
(d) p-nitroaniline (Maurin, J.; Krygowski, T. M. *J. Mol. Struct.* 1988, 172, 413).