

LA-UR-95 95-1975

Title:

A MOLECULAR ARCHITECTURAL APPROACH TO
SECOND-ORDER NONLINEAR OPTICAL MATERIALS

02,642

Author(s):

Xiaoguang Yang, CST-4
Duncan McBranch, CST-6
Basil Swanson, CST-4
DeQuan Li, CST-4

Submitted to:

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Los Alamos
NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. 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 under the auspices of the U.S. Department of Energy.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED 35

MASTER

Form No. 836 R5
ST 2629 10/91

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

A MOLECULAR ARCHITECTURAL APPROACH TO SECOND-ORDER NONLINEAR OPTICAL MATERIALS

Xiaoguang Yang, Duncan McBranch, Basil Swanson, and DeQuan Li*

The Chemical Science and Technology Division (CST-4 and CST-6), Los Alamos National Laboratory, Los Alamos, NM 87545

ABSTRACT

The design and synthesis of a family of calix[4]arene-based nonlinear optical (NLO) chromophores are discussed. The calixarene chromophores are macrocyclic compounds consisting of four simple D- π -A units bridged by methylene groups. These molecules were synthesized such that four D- π -A units of the calix[4]arene were aligned along the same direction with the calixarene in a cone conformation. These nonlinear optical super-chromophores were subsequently fabricated into covalently bound self-assembled monolayers on the surfaces of fused silica and silicon. Spectroscopic second harmonic generation (SHG) measurements were carried out to determine the absolute value of the dominant element of the nonlinear susceptibility, χ_{zzz} , and the average molecular alignment, ψ . We find a value of $\chi_{zzz} \sim 1.5 \times 10^{-7}$ esu (60 pm/V) at a wavelength of 890 nm, and $\psi \sim 36^\circ$ with respect to the surface normal.

INTRODUCTION

Organic nonlinear optical (NLO) materials offer great potential for use in integrated optical devices. NLO thin-film materials have been fabricated by Langmuir-Blodgett (LB) techniques,¹ molecular self-assembly,² and electric field poling of functional polymers.³ The critical issue, however, remains the stability of the acentric alignment of the NLO chromophores. We report here a molecular architectural approach to thin films aimed at achieving stable materials for NLO applications. The key strategy is to fix chromophore orientation at the molecular level by structural interlocking of dipolar molecules into cone-shaped supermolecules, and then to use these to build polar self-assembled monolayers.

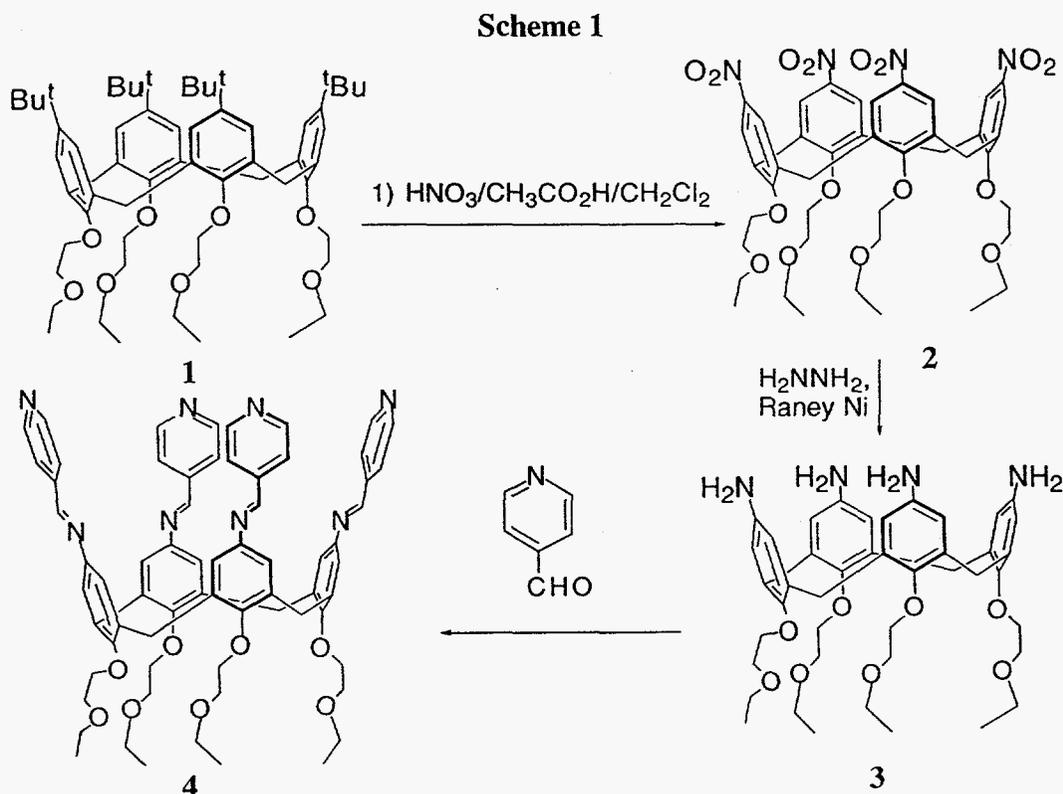
The surface molecular building blocks are calix[4]arene derivatives, which consist of four NLO chromophore units bridged by methylene groups. The chromophores are stilbazole derivatives with a D- π -A structure, where D and A are electron donating and accepting groups, respectively, and π is a π -conjugated segment. This structural feature has been widely used to attain large values of the molecular second-order nonlinear susceptibility, β . Reinhoudt *et al* have recently reported the study of poled neat calixarene films and calixarene-doped polymeric films for second-order nonlinear optics.⁴ They showed that "cone" conformation calix[4]arene chromophores exhibit large values of the electro-optic coefficient d_{33} (6-11 pm/V at 30-60% wt) with a high degree of orientation. In this paper, we report the synthesis and characterization of

NLO calix[4]stilbazole imine derivative with the calixarene frozen in a cone conformation. Furthermore, we discuss the construction of monolayers of the calixarene via covalent bonding to the silylated oxide surface, and second harmonic generation measurements on these self-assembled monolayer thin films. We find larger values of d_{33} ($d_{33} \sim 60$ pm/V at $\lambda = 890$ nm).

RESULTS AND DISCUSSION

1. Design and Synthesis of Calixarene-Based NLO Chromophores

Although many functionalized calixarenes have been synthesized,⁵ preparation of calix[n]stilbazole ($n = 4, 6, 8$) and its derivatives has been proven to be more difficult. The major synthetic considerations are the solubility and the conformation freezing of the calixarenes. Our synthetic strategy is to first freeze the calixarene in a cone conformation by substituting the lower rim of the calix[4]arene and then functionalize the upper rim of the calixarene for the incorporation of pyridyl units. The synthesis of imine derivative of calix[4]stilbazole is depicted in scheme 1. Compound (1) and (2) were synthesized according to literature procedures.^{6,7} Reduction of nitrocalixarene (2) gave *p*-aminocalix[4]arene (3). The condensation of *p*-aminoethoxyethylether-

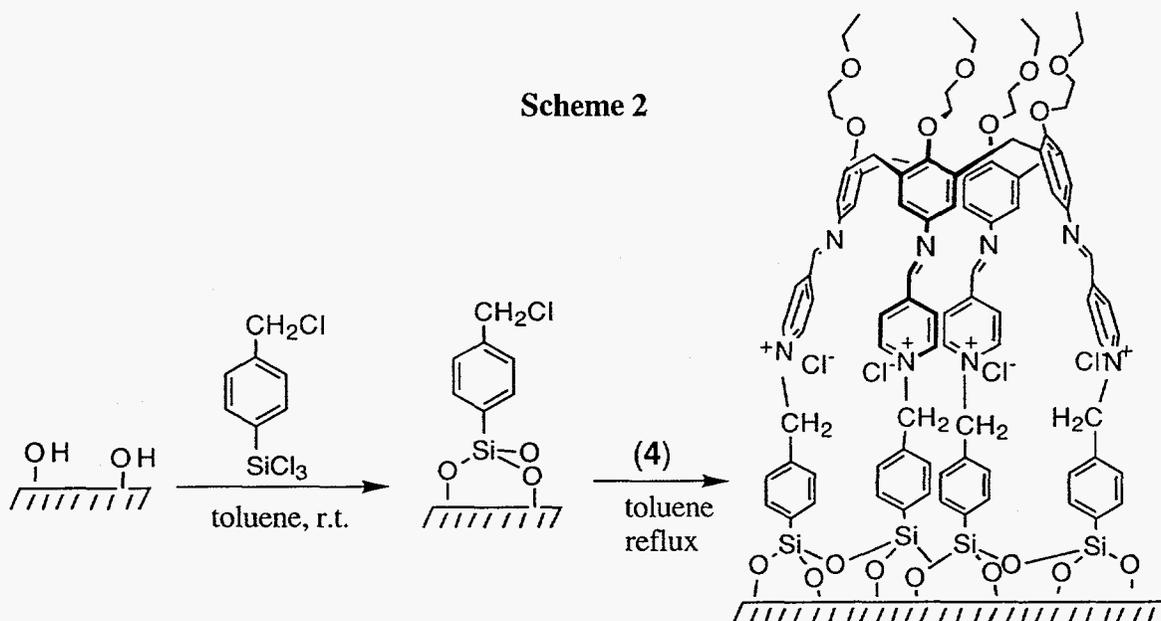


calix[4]arene (3) with 4-pyridylcarboxaldehyde gave the desired NLO chromophore (4). All the structures were confirmed by ^1H NMR and IR data. A proton ^1H NMR spectrum of (4) in CDCl_3

indicated that (4) has a rigid “cone” conformation with the D- π -A dipolar units aligned in the same direction; this was manifested by the fact that bridging methylene protons split into two doublets with strong coupling between them ($J = 15$ Hz).⁵ The presence of long ethoxyethyl groups prevents flip-over of the individual rigid rod-like stilbazole units in (4) and the “cone” conformation is virtually frozen at room temperature. It is noteworthy, however, that the condensation reaction failed when the formyl and amino groups are switched.

2. Construction of Self-assembled Monolayer of (4)

The construction of self-assembled monolayers of (4) is based on the approach reported by Li *et al.*^{2a} Silicon wafer and fused silica substrates were treated with a silane coupling agent *p*-chloromethylphenyltrichlorosilane in either toluene or chloroform for 24 h, followed by a incubation of silylated substrate in 1 mM of compound (4) in toluene at 110 °C for three days. The monolayer was thoroughly cleaned by sonication in CHCl_3 , followed by vigorous rinsing with CHCl_3 to remove any noncovalently bonded surface species.



The self-assembled monolayers consisting of pyramid-like imine derivative of calix[4]stilbazole were characterized by surface polarized FTIR using internal attenuated total reflection (ATR) within a Ge hemisphere crystal with *p*-polarization at 45 degree of incidence. The formation of covalent C-N bonds between the calix[4]stilbazole imine and the silane anchoring layer was revealed by the presence of pyridinium species ($\nu = 1635$ cm^{-1}) on the surface. The fact that no pyridine mode at 1595 cm^{-1} was observed indicates that the surface quaternization is complete leaving no dangling stilbazole imine structures in the self-assembled monolayer.⁸ The electronic absorption spectrum of the monolayer exhibits a characteristic charge transfer transition

at 390 nm (Figure 1), which is consistent with the observation of the pyridinium mode; both indicate successful quaternization reaction. The absorption peak of the monolayer red-shifted to 390 nm from 350 nm is also consistent with the presence of stronger electron withdrawing groups (pyridinium vs. pyridyl group) in the film. The optical absorptions from both surface IR ($A_{1635\text{ cm}^{-1}} = 2 \times 10^{-3}$) and UV-vis ($A_{390\text{ nm}} = 3.5 \times 10^{-3}$) suggests that the thin-film thickness for these calix[4]stilbazolium is on the order of a typical single monolayer taking into account of the chromophore orientation effects.

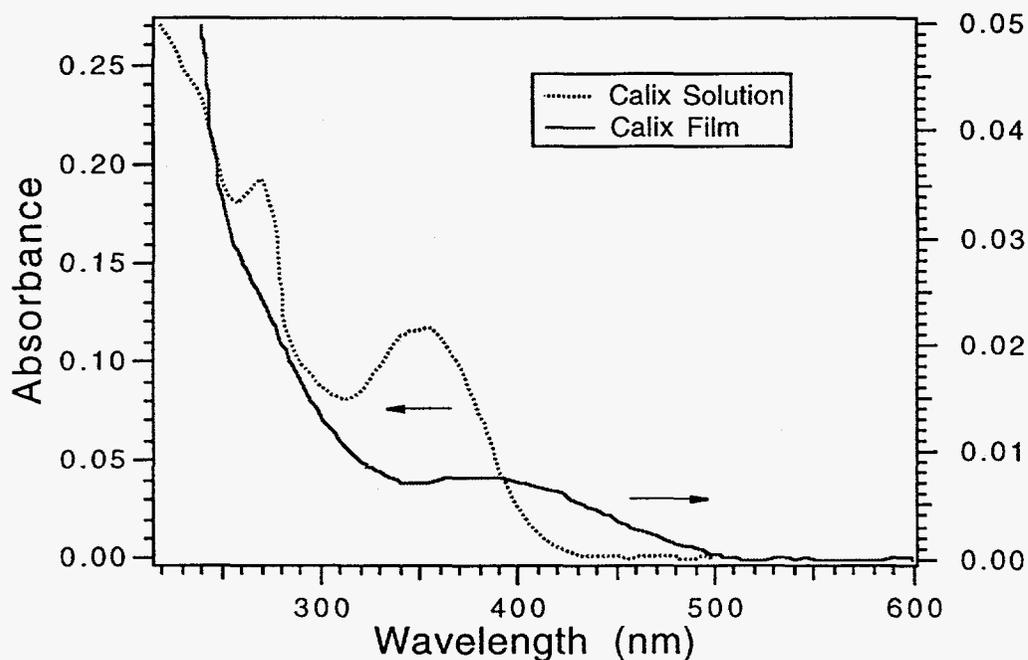


Figure 1. UV-vis absorption spectra of the imine derivative of calix[4]stilbazole (4) in methanol (dotted line) and the imine derivative of calix[4]stilbazolium on SiO₂ substrate (solid line), respectively.

3. Spectroscopic Second Harmonic Generation Measurements

Second harmonic generation (SHG) was measured for fundamental wavelengths between 890 nm and 750 nm. The laser source was a passively mode locked Ti:Sapphire laser (Coherent Mira) operating in either femtosecond (150 fs autocorrelation width) or picosecond (2 ps width) mode, with 100 MHz repetition rate. The SHG signal was measured as a function of incident angle for *p*-polarized SHG, and both *s*- and *p*-polarized fundamental. The SHG light was filtered from the fundamental with a combination of glass filters (Schott BG-39) and a single-grating monochromator. Light was detected with a cooled photomultiplier tube, by synchronous detection with a digital lockin amplifier referenced to a chopper in the fundamental beam path.

In the cone-shaped symmetry (C_{∞}), there are only two independent elements of the second-order nonlinear susceptibility, χ_{zzz} and $\chi_{zxx} = \chi_{zyy}$, in these self-assembled monolayers.

To determine the values of the second-order nonlinear susceptibility, the ratio of χ_{zzz} to χ_{zxx} was first derived by comparison of the angular dependence of the measured *p*-polarized SHG from *p*-polarized fundamental versus *s*-polarized fundamental.⁹ The absolute χ_{zzz} values were then deduced by comparison with SHG measured from a Y-cut quartz crystal, with fundamental polarization along the optic axis. Figure 2 shows the angular dependence of the measured

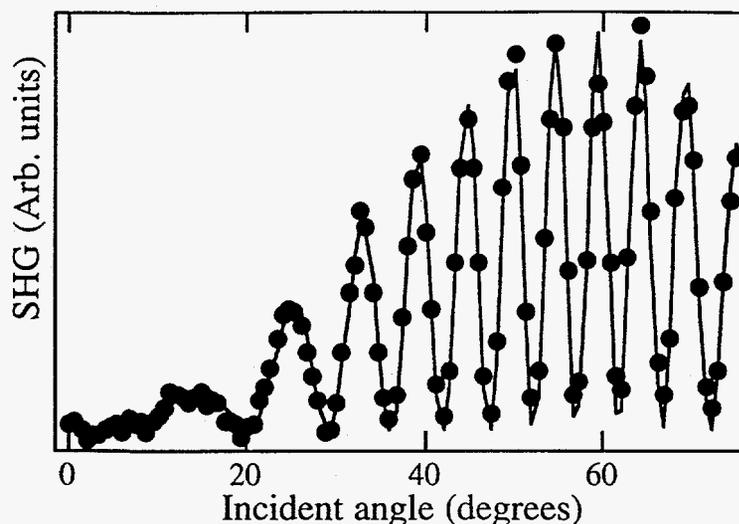


Figure 2. SHG signal vs. incident angle for *p*-polarized SHG from *p*-polarized fundamental at a wavelength of 890 nm (solid circles), plotted together with best fit (solid line, see text).

SHG for *p*-polarized fundamental, and *p*-polarized SHG, for the imine derivative of a calix[4]stilbazole monolayer at a fundamental wavelength of 890 nm. In Figure 2, the data for 2 ps pulses are shown along with the theoretical best fits. There are two important features in this data: the overall envelope shape, which is determined by the orientation of the individual molecules ($\psi \sim 36^\circ$) in the monolayer relative to the surface normal,^{2b,10} and the interference fringes, which arise from the two identical monolayers on opposite sides of the fused silica substrate.^{2a} For the 1 mm fused silica samples considered here, effects of pulse walkoff due to mismatched group velocities of the fundamental and SH pulses can be neglected. The solid line in Figure 2 is the best fit to an expression developed in Ref. 2, modulated by the interference term, which has the same physical origin and angular dependence as the well-known Maker fringes in bulk samples.¹¹ These data indicate that the average orientation of the stilbazole chromophores is 36° relative to the surface normal, and that the absolute magnitude of $\chi_{zzz} \sim 1.5 \times 10^{-7}$ esu ($d_{33} \sim 60$ pm/V), at a wavelength of 890 nm. The wavelength dependence indicates a gradual increase of $\chi^{(2)}$ as the fundamental moves to shorter wavelength, with an absence of any resonant peaks, consistent with normal refractive index dispersion in this nonresonant region.

CONCLUSION

We have synthesized a calix[4]arene-based NLO chromophoric building block and constructed covalently bound self-assembled monolayers on Si wafers and SiO₂ substrates. We have made a significant step forward in molecular architecture by demonstrating the formation of self-assembled monomolecular layer of "pyramid"-like structures. Structural interlocking via the

bridging methylene groups among the D- π -A units yields improved stability, exceptional large second order nonlinearities ($d_{33}\sim 60$ pm/V), and optimized molecular dipole alignment. Spectroscopic $\chi^{(2)}$ measurements were carried out in the near infrared region and two photon resonance enhancement was found to be minimal. We have demonstrated that using molecular chromophores pre-assembled into supermolecules to achieve fixed orientation at the molecular level is a viable approach to the construction of polar self-assembled monolayers. We are currently pursuing substitutions at both ends of the calix[4]arene NLO chromophores in attempt to construct multilayer molecular films for nonlinear optical studies.

ACKNOWLEDGMENTS

This research was performed under the auspices of the Department of Energy. The authors acknowledge the support of the Center for Materials Science at Los Alamos National Laboratory and the Laboratory Directed Research and Development program. X. Y. acknowledges the support of a Los Alamos Director's Postdoctoral Fellowship. We thank D. Logsdon, W. Archer at the glass shop of LANL for technical assistance.

REFERENCES

1. G. L. Ashwell, P. D. Jackson, W. A. Crossland, *Nature* **368**, 438 (1994)
2. (a) D. Li, M. A. Ratner, T. J. Marks, C. H. Zhang, J. Yang, G. K. Wong, *J. Am. Chem. Soc.* **112**, 7389 (1990). (b) H. E. Katz, G. Scheller, T. M. Putvinski, M. L. Schilling, W. L. Wilson, C. E. D. Chidsey, *Science* **254**, 1485 (1991).
3. M. Eich, G. C. Bjorklund, D. Y. Yoon, *Polym. Adv. Tech.* **1**, 189 (1990).
4. (a) E. Kelderman, L. Derhaeg, G. J. T. Heesink, W. Verboom, J. F. J. Engbersen, N. F. Hulst, A. Persoons, D. N. Reinhoudt, *Angew. Chem. Int. Ed. Engl.* **31**, 1075 (1992). (b) E. Kelderman, G. J. T. Heesink, L. Derhaeg, T. Verbiest, P. T. A. Klaase, W. Verboom, J. F. J. Engbersen, N. F. Hulst, K. Clays, A. Persoons, D. N. Reinhoudt, *Adv. Mater.* **5**, 925 (1993).
5. C. D. Gutsche, *Calixarenes*, (Royal Society of Chemistry, 1989).
6. S. -K. Chang, I. Cho, *J. Chem. Soc. Perkin Trans. 1*, 211 (1986).
7. W. Verboom, A. Durie, R. J. M. Egberink, Z. Asfari, D. N. Reinhoudt, *J. Org. Chem.* **57**, 1313 (1992).
8. D. Li, C. T. Buscher, B. I. Swanson, *Chem. Mater.* **6**, 803 (1994).
9. D. Li, B. I. Swanson, J. M. Robinson, Mark A. Hoffbauer, *J. Am. Chem. Soc.* **115**, 6975 (1993).
10. T. Zhang, C. Zhang, G. K. Wong, *J. Opt. Soc. Am. B.* **7**, 902 (1990).
11. P. D. Maker, R. W. Terhune, M. Nisenoff, C. M. Savage, *Phys. Rev. Lett.* **8**, 21 (1962).