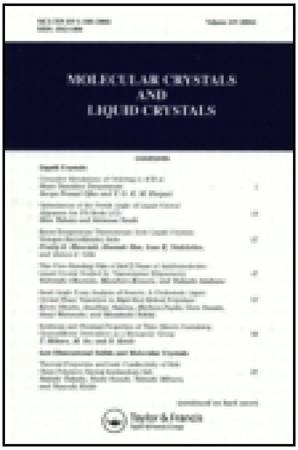

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The Effect of Chromophore Architecture and Deposition Conditions on the Optical and Microstructural Characteristics of Self-Assembled Chromophoric Thin Film NLO Materials

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THE EFFECT OF CHROMOPHORE ARCHITECTURE AND DEPOSITION CONDITIONS ON THE OPTICAL AND MICROSTRUCTURAL CHARACTERISTICS OF SELF-ASSEMBLED CHROMOPHORIC THIN FILM NLO MATERIALS.

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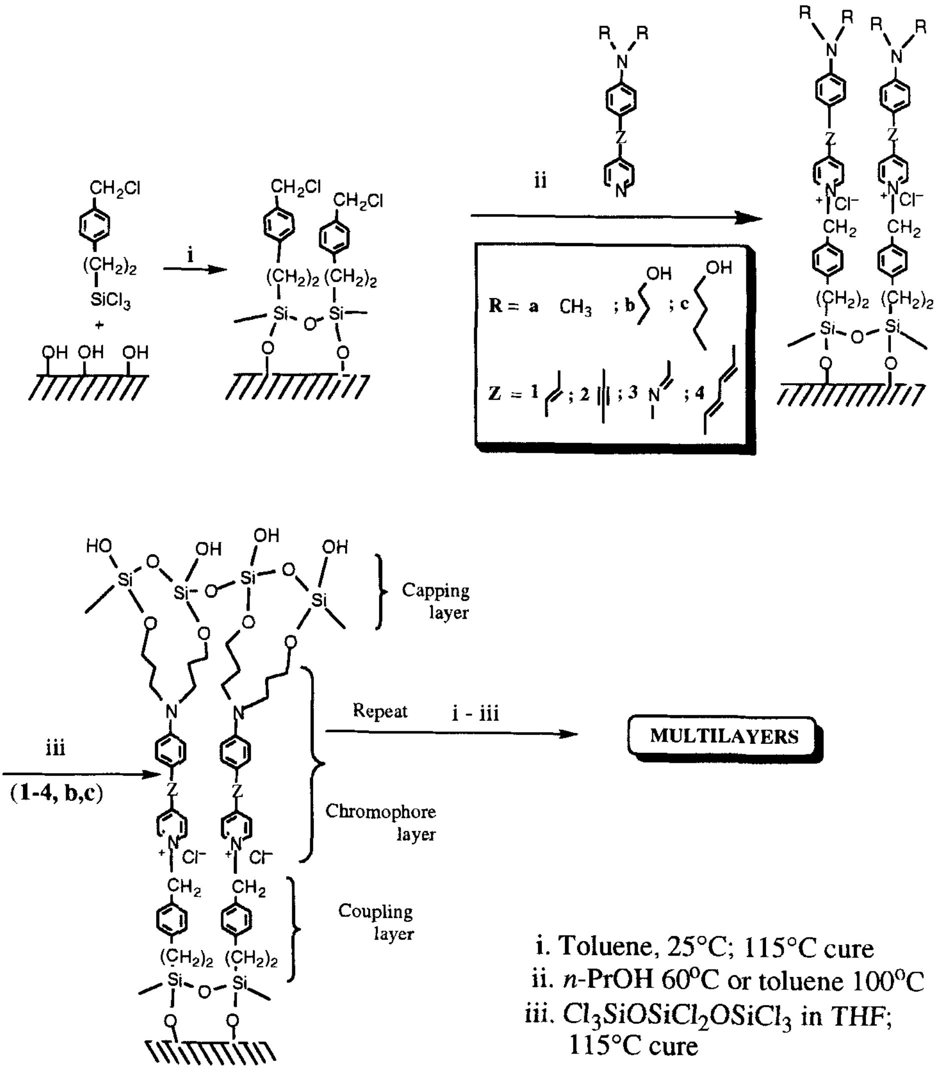
Abstract Construction on inorganic oxide substrates of covalently self-assembled second-order nonlinear optical (NLO) materials containing a variety of acentrically organized high-β chromophores is investigated as a function of film deposition conditions. Structurally different chromophores exhibit varying packing arrangements on the surface. Changing the medium for the chromophore deposition reaction on functionalized surfaces from a polar solvent to a nonpolar solvent and raising the temperature increases the chromophore number density on the surface and yields improved NLO response. These robust thin film materials show very high second harmonic generation (SHG) efficiencies with $\chi^{(2)}_{zzz}$ for ~ 25 Å thick monolayers of up to 7×10^{-7} esu at 1064 nm.

INTRODUCTION

We recently reported[1] a new approach to the construction of second-order nonlinear optical (NLO) materials[2] which involves the covalent self-assembly of multilayers of high-β chromophores on inorganic oxide supports. Such robust thin film superlattices exhibit high second harmonic generation (SHG) efficiencies with $\chi^{(2)}_{zzz}$ values for 25 Å thick monolayers of 2-7 x 10^{-7} esu. This level of response is higher than conventional inorganic oxides such as $LiNbO_3$, and is comparable to the most efficient poled polymers and acentric Langmuir-Blodgett films.[2,3] In addition, the self-assembled thin films are thermodynamically equilibrated systems which do not require an external aligning electric field to establish and maintain an acentric environment. This represents a major advance over poled NLO polymers where inducing and completely stabilizing net chromophore alignment remains a daunting challenge.[2,3] In this contribution, we survey key aspects of thin film construction, focusing on structural variation of chromophore building blocks and the deposition conditions for multilayer construction. We demonstrate how these crucial variables affect microstructural features such as surface coverage, average chromophore tilt angle, and NLO properties of the resulting films.

Scheme I



i. Toluene, 25°C; 115°C cure
ii. *n*-PrOH 60°C or toluene 100°C
iii. $Cl_3SiOSiCl_2OSiCl_3$ in THF; 115°C cure

Construction of Self-Assembled Thin Films.

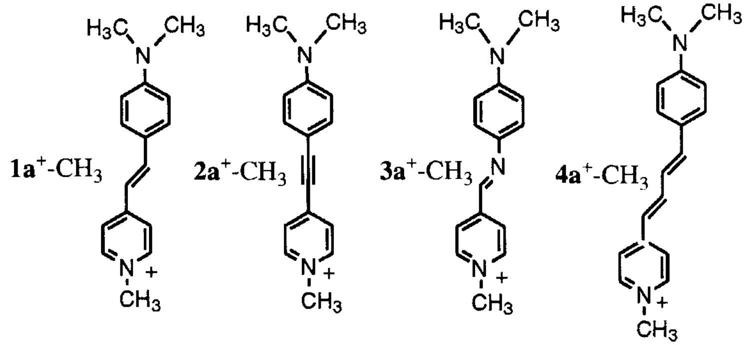
The general synthetic strategy (Scheme I) for molecular self-assembly is based on siloxane condensation methodology originally developed by Sagiv.[5] Clean glass substrates (a similar procedure can also be applied to ITO-coated glass, mica, as well as single crystal silicon and germanium with native oxide layers) are immersed in a toluene solution of 1-chloromethyl-4-(2-trichlorosilylethyl)benzene (coupling agent) at room temperature for 15 min to 36 h, and the resulting monolayers air-cured at 115 °C for 15 minutes (Scheme I, step *i*). Chromophore[6] deposition is carried out by immersion of these functionalized substrates in a variety of solvents including *n*-PrOH, THF/toluene, and toluene at 60, 80, and 100°C respectively (step *ii*, Scheme I) for 2-4 days. Treatment of the chromophore-functionalized substrates (**1**-**4**, R = **b**,**c**) with octachlorotrisiloxane (capping agent, step *iii*) introduces transverse crosslinking and exposes Si-OH moieties resembling the original glass surface. The process can then be repeated to construct multilayered structures. Using this methodology, we have constructed superlattices[1b] with up to 9 layers. Evolution of the surface structures is monitored by contact angle measurements which repeat in the sequence (Scheme I) original glass surface, 15°; *i*, 74°; *ii*, 46°; *iii*, 18°, and are in accord with expected surface wettabilites; by XPS - the original signal at 205 eV for Cl_{2p} (Scheme I, step *i*) of the coupling agent shifts to 203 eV and a signal at 400 eV for N_{1s} appears (step *ii*); by UV-Vis spectroscopy which reveals large shifts in λ_{max} upon quaternization (from 390 to 509 nm for monolayers based on **1**); by polarized second harmonic generation (vide infra), and also by grazing angle X-ray reflectivity. These films are insoluble in common organic solvents and most acids, and can only be removed by etching with HF solution or diamond polishing.

RESULTS AND DISCUSSION

Chromophore design

The first challenge in the molecular self-assembly of NLO materials is the identification of component molecules having suitable reactivity and structures for the process, as well as having high molecular hyperpolarizabilities (β). The noteworthy features of bifunctional chromophore precursors (Scheme I, **1-4**, **b**-**c**) include a derivatized amino donor group separated by tunable π-conjugation length from a 4-pyridyl functionality. The latter becomes a strong electron acceptor only upon quaternization. The calculated off-resonance (fundamental at $\hbar\omega$ = 0.65 eV, SHG at 950 nm) molecular hyperpolarizabilities of the model dimethylamino chromophores based on **1-4** together with their calculated and experimental absorption maxima (in dilute methylene chloride solutions) are shown in Scheme II. Such molecules possess very high β values (these

Scheme II



$\beta_{zzz}^{calcd.}$ ($\times 10^{-30}$ esu)	178	171	92	343
$\lambda_{max}^{calcd.}$ (nm)	479	466	400	526
$\lambda_{max}^{expt.}$ (nm)	512	470	516	498

should be compared[4] with molecules such as *p*-nitroaniline, where $\beta_{vec}^{calcd} = 10 \times 10^{-30}$ cm^5 esu^{-1} at $\hbar\omega = 0.65$ eV, and *p*-aminophenyl-4-nitrobenzene, where $\beta_{vec}^{calcd} = 46 \times 10^{-30}$cm^5 esu^{-1} at $\hbar\omega = 0.65$ eV), arguing that properly organized assemblies of these molecules should exhibit very high bulk nonlinearities. These computational results also indicate that replacing the conjugated double bond bridge in **1** with the triple bond in **2** should yield comparable $\beta_{vec.}$ values, and a λ_{max} which is significantly blue-shifted when anchored to the surface (see also Table I). The latter should afford greater optical transparency.

SHG properties of self-assembled films.

Polarized SHG measurements were carried out in the transmission mode by placing the functionalized glass slides in the path of the p-polarized light of a Nd:YAG laser operating at 1064 nm. No in-plane anisotropy of the SHG signal is observed when the slides were rotated about the film normal, which indicates that the films possess uniaxial symmetry and that the distribution of chromophore molecular orientations does not have an azimuthal dependence. Fig. 1 shows a typical angle-dependent SHG signal intensity plot obtained from a glass slide coated on both sides with a chromophoric (**3a**) self-assembled monolayer. The interference pattern (Fig. 1) is due to the phase difference between the two SHG waves generated at either side during the propagation of the fundamental wave. The complete destructive interference indicates that the quality of the films on the two sides is uniform and nearly identical.

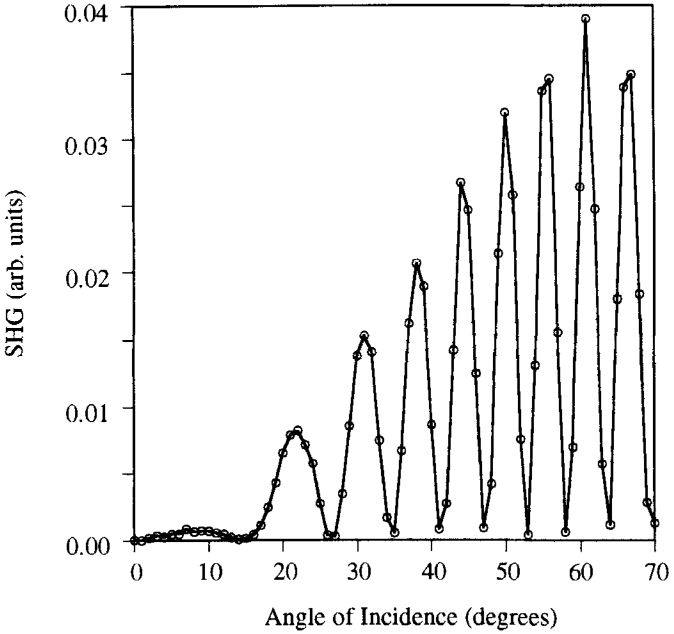


FIGURE 1. SHG intensity ($I^{2\omega}_{p\text{-}p}$) as a function of fundamental beam incident angle of a glass slide having a self-assembled **3a**-derived monolayer on either side.

The values of the SHG coefficient and tilt angles for the monolayers based on **1-4** together with their absorption spectral maxima are given in Table I. These monolayers were constructed with 15 min coupling agent reaction time (step *i*, Scheme I) for **1a**, **3a**, and **4a**. Under these reaction conditions, the rigid rod alkynyl chromophore **2a** showed very poor SHG response, and a coupling agent deposition of at least 10h was necessary[1d] for a comparable SHG response. The chromophore quaternization/anchoring to the surface (step *ii*, Scheme I) was performed in *n*-PrOH at 60°C for 48h for **1a**, **2a**, and **4a** and in toluene at 100°C for 48h in the case of **3a** (due to the possible hydrolytic instability of chromophore **3a** in protic polar solvents).

The chromophore tilt angle from the surface normal, Ψ, was calculated[7] by fitting the ratio of $\chi^{(2)}$ tensor components to the experimental data using the relationship $\chi^{(2)}_{zzz}$) / $\chi^{(2)}_{yyz} = 2\cot^2\Psi$. The chromophore number density on the surface, N_S, was calculated using the equation $(\chi^{(2)}_s)_{\perp\perp\perp} = N_S \cos^3\Psi\ \beta^{calcd}_{zzz}$; here $(\chi^{(2)}_s)_{\perp\perp\perp}$ is the surface nonlinear susceptibility, and the β^{calcd}_{zzz} are the values calculated[4] at 1064 nm. The results in Table I show that for films prepared with short coupling agent reaction times

TABLE I Linear absorption, SHG efficiency, chromophore tilt angle, and chromophore surface density data for self-assembled monolayers based on chromophores **1a**-**4a**.

Chromophore	$\lambda_{max}^{monolayer}$ (nm)	$\chi_{zzz}^{(2)}$ ($\times 10^{-7}$ esu)	$\bar{\Psi}$ (°)	N_S ($\times 10^{14}$ molec's/cm^2)
1a	509	2.2	39 ± 2	1.23
2a	472	1.0	43 ± 2	0.87
3a	538	1.3	39 ± 2	1.15
4a	520	1.9	35 ± 2	0.43

(15 min), there is a relatively low coverage of chromophore molecules on the surface: **1a** and **3a** ~ 80 Å^2/molecule; **2a** ~ 115 Å^2/molecule (for 10h reaction time); and **4a** ~ 230 Å^2/molecule. Comparison of the optical spectra of the various chromophores in dilute CH_2Cl_2 solution to those of the corresponding self-assembled films reveals no shifts in maxima for chromophores **1a** and **2a**, and a bathochromic shift of about 30 nm for chromophores **3a** and **4a**. This observation indicates that at relatively low coverage, chromophores **1a** and **2a** are dispersed fairly uniformly on the surface as isolated dipoles. However, chromophores **3a** and **4a** appear to be arranged in clusters (dimers, trimers, etc.) with intermolecular π–π interaction of the transition dipoles[8]. It is worth noting that high-β_{vec} chromophore **4a**, which exhibits the lowest surface coverage, has a $\chi^{(2)}$ comparable to chromophore **1b**, which has the highest chromophore density under these deposition conditions.

Optimization of the self-assembly processes

We have recently found[1a] that, for the construction of monolayers based on chromophore **1b**, changing the coupling agent deposition procedure (step *ii*, Scheme II) to a multistep process resulted in thin films with much higher chromophore surface densities (based on the SHG response of the resulting films). In such a reaction sequence, the clean glass substrates are treated with the coupling agent for 18h at room temperature, removed from the reaction flask, washed with toluene under air, and reimmersed in the coupling agent solution for another 18h at ambient temperature. Chromophore deposition (step *ii*, Scheme I) was than investigated for **1b** and **1c** in *n*-PrOH (4 days, 60°C), 1:1 THF/toluene (4 days, 80°C), and toluene (4 days, 100°C). Significant side reactions of the chromophore precursor were observed in *n*-PrOH. The properties of monolayers prepared in these experiments are summarized in Table II.

TABLE II SHG and packing properties of self-assembled monolayers prepared from chromophores **1b** and **1c**.

Chromophore	**1b**			**1c**		
Solvent	$\chi^{(2)}_{zzz}$ ($\times 10^{-7}$ esu)	$\bar{\Psi}$ (°)	N_S ($\times 10^{14}$ molec's/cm^2)	$\chi^{(2)}_{zzz}$ ($\times 10^{-7}$ esu)	$\bar{\Psi}$ (°)	N_S ($\times 10^{14}$ molec's/cm^2)
n-PrOH	3.1	40 ± 2	1.8	3.0	39 ± 2	1.7
THF/toluene [1:1]	4.1	39 ± 2	2.3	3.9	41 ± 2	2.4
Toluene	7.0	36 ± 2	3.5	5.1	42 ± 2	3.3

A number of observations are noteworthy: (a) changing the solvent for the chromophore deposition reaction (step *ii*, Scheme I) from a protic polar solvent (*n*-PrOH) to an aprotic polar-nonpolar solvent mixture (THF/toluene), to a nonpolar solvent (toluene), and increasing the reaction temperature, results in films with greater NLO response; (b) the approximate relative chromophore surface densities (based on calculated β_{zzz} values at 1064 nm) are much higher for the monolayer prepared in toluene (~ 30 Å^2/molecule) than for those prepared in THF/toluene (~ 42 Å^2/molecule) or those prepared in *n*-PrOH (~ 56 Å^2/molecule); and (c) a comparison of the data on monolayers prepared in toluene using chromophore **1b** (having an even number of methylene units) with those based on **1c** (having an odd number of methylene units) shows that the SHG efficiency of the former films are higher than the latter. The higher $\chi^{(2)}_{zzz}$ for the monolayers based on **1b** may be due to higher chromophore surface coverage and also to a different packing arrangement of these chromophores on the surface. The average chromophore tilt angle for **1b** (36 ± 2°) is significantly smaller than that of chromophore **1c** (42 ± 2°). This indicates that chromophores **1b** are aligned more along the surface normal and hence, with comparable surface densities to **1c** ($N_S = 3.3 \times 10^{14}$ molec's/cm^2; 30 Å^2/molecule for **1c** versus $N_S = 3.5 \times 10^{14}$ molec's/cm^2; 29 Å^2/molecule for **1c**), the larger value of $\chi^{(2)}_{zzz}$ for **1b** results from more "vertical" packing characteristics of the chromophore. This "odd-even methylene number packing effect" is commonly observed in liquid crystals[9]. Here, this effect becomes significant only at high chromophore coverage and on surfaces where intermolecular packing forces dominate the structure.

CONCLUSIONS

Molecular self-assembly of a variety of organic chromophores with large molecular hyperpolarizabilities and varying electronic and geometrical requirements is a new technique for the construction of thin film superlattices with very large and tailorable second-order NLO responses. The chromophore surface densities in these thin films are dependent on building block architecture and the film deposition conditions, which have a significant effect on packing and the SHG characteristics of the resulting films. For optimized thin film construction, longer coupling agent reaction times and chromophore anchoring/quaternization in nonpolar solvents such as toluene at elevated temperatures, produce films with much larger $\chi^{(2)}_{zzz}$ values. It is noteworthy that a $\chi^{(2)}_{zzz}$ value of 2×10^{-6} esu is expected for monolayers based on **4a** with chromophore surface densities comparable to those of the stilbazolium chromophore. Incorporation of these chromophores and implementation of the above processes in the multilayer construction are currently being pursued.

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