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Peter Gölitz, Editor

Layer-By-Layer Deposition and Ordering of Low-Molecular-Weight Dye Molecules for Second-Order Nonlinear Optics**

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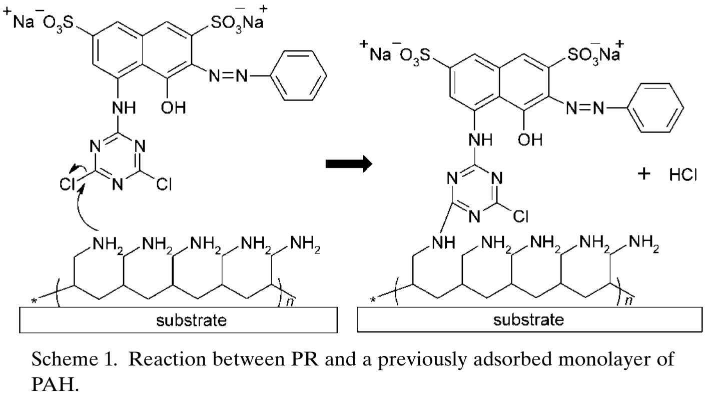
Materials that exhibit second-order nonlinear optical (NLO) properties are key components in electrooptic modulators and frequency-doubling devices.[1] Second-harmonic generation (SHG), in which incident light at one frequency is converted into light at twice that frequency, is one example of second-order NLO phenomena and is often used as an experimental probe of the second-order susceptibility ($\chi^{(2)}$). A material must have a non-centrosymmetric structure to possess a nonzero $\chi^{(2)}$. Electrooptic modulators have traditionally employed ferroelectric inorganic crystals, such as lithium niobate or potassium dihydrogen phosphate, which are formed at high temperatures. However, organic NLO materials offer several advantages in performance, such as higher nonlinear susceptibilities, higher modulation rates, and potentially lower device fabrication costs.[2] Organic films exhibiting nonzero $\chi^{(2)}$ values have been fabricated using a variety of methods, including electric field poling,[3] Langmuir–Blodgett (LB) films,[4] and covalent self-assembly.[5] Both poled polymer systems and LB films have been made with non-centrosymmetric structures that exhibit relatively high values for $\chi^{(2)}$, but poor temporal or mechanical stability restrict their potential applications.[6] Deposition processes using reactive silane compounds require organic solvents and high temperatures.[5]

There is a large and growing body of literature on the use of layer-by-layer (LBL) methods for fabricating nanostructured films for a variety of applications. The LBL technique, which relies on purely electrostatic interactions, was first developed by Iler[7] and further elaborated upon by Decher et al.[8] Several research groups have demonstrated that the NLO films made by this technique have greater thermal and temporal stability than poled polymer systems.[9] A related approach that could be employed to fabricate NLO materials involves the use of low-molecular-weight dye molecules and polyelectrolytes as film constituents. Yamada et al. made films of poly(diallyldimethylammonium chloride) and Erichrome Black T that exhibited an SHG intensity that increased only for the first five bilayers and then reached a plateau.[10] Other research groups, including ourselves, have found that ionic interactions alone are not sufficient for constructing LBL films with low-molecular-weight chromophores.[11] A combination of low-molecular-weight chromophoric molecules and polyelectrolytes that could be used to construct stable NLO films with the large number of bilayers needed for electrooptic devices is yet to be demonstrated.

The objective of this work was to demonstrate that LBL films made under ambient conditions with a water-soluble, monomeric chromophoric molecule can possess high net polar ordering in each bilayer. By alternating the methods of deposition for each monolayer (covalent reaction and electrostatic interaction) and decoupling the chromophore orientation from the steric constraints of a polymer chain, we hypothesized that the non-centrosymmetric orientation required for nonzero $\chi^{(2)}$ values could be achieved.

The model anionic/reactive species used in this study was Procion Red MX-5B (PR), and the NLO-inactive polycation was poly(allylamine hydrochloride) (PAH, Scheme 1). The pH values of the dipping solutions determine the ionization state of the amine moieties on PAH, which affects both the conformation of the polymer upon adsorption and its subsequent reactivity with PR. Efficient electrostatic deposition of PAH requires that the pH value of the PAH solution is maintained near or below the pK_a value of the amino group



Scheme 1. Reaction between PR and a previously adsorbed monolayer of PAH.

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(8.7),[12] where the majority of the NH_2 groups will be protonated and available for interaction with negative charges on the substrate or the PR molecule. The pH value of the PR solution must be near or above the pK_a value of the PAH amine groups for efficient covalent attachment of the chromophore to the dichlorotriazine ring at room temperature.[13]

In situ measurements of SHG intensity during PR deposition showed that each monolayer was deposited within two minutes at room temperature. Successful film growth was characterized by a linear increase in the absorbance and thickness with the number of bilayers deposited (Figure 1 and Table 1). The pH value of the PAH solutions in these experiments was held at either 4.5 or 7.0. The positive charges along the PAH chain strongly repel each other and are strongly attracted to the negatively charged surface. These two effects lead to the deposition of PAH in layers with a bilayer thickness less than 1 nm.

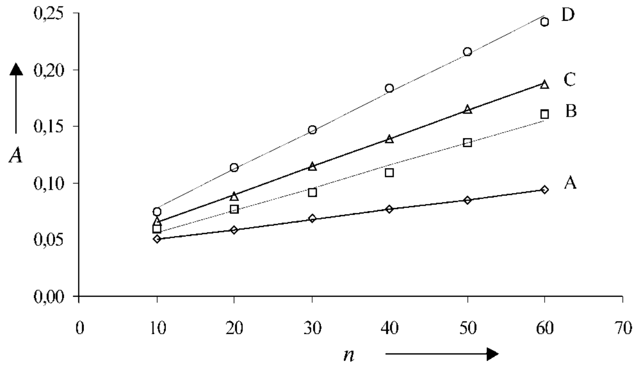

Figure 1. Absorbance (A) at 538 nm as a function of the number of bilayers (n) in PR–PAH films. Experimental conditions for A–D correspond to entries in Table 1. Lines are obtained by linear regression analysis. ◇: PAH pH 4.5/PR pH 7.0, □: PAH pH 4.5/PR pH 10.5, △: PAH pH 7.0/PR pH 7.0, ○: PAH pH 7.0/PR pH 10.5.

The pH value of the PR solution has a significant effect on the amount of chromophore incorporated into the film. When the pH value of the PAH solution was held constant at 4.5 or 7.0 and that of the PR solution was increased from 7.0 to 10.5, the amount of PR deposited per bilayer increased, which is consistent with the increased covalent-coupling efficiency. When the pH value of the PR solution was 10.5 and that of the PAH solution was increased from 4.5 to 7.0 (compare experiments B and D), a statistically insignificant increase in the film thickness per bilayer ($p > 0.05$) was observed. However, this also resulted in a small but significant increase in the amount of PR deposited per bilayer ($p < 0.05$), as measured by the absorbance per bilayer.

Table 1. Properties of films made by a hybrid deposition process from Procion Red (PR) and poly(allylamine hydrochloride) (PAH).

Expt	PAH pH	PR pH	$A n_b^{-1}$[a]	t_b [nm][b]	$\chi^{(2)}$ [$\times 10^9$ esu][e]	Rel. $A n_b^{-1}$[c]	Rel. $(I_{2\omega})^{1/2} n_b^{-1}$[c]
A	4.5	7.0	$(8.9 \pm 0.1) \times 10^{-4}$	[d]	–	–	–
B	4.5	10.5	$(2.0 \pm 0.1) \times 10^{-3}$	0.34 ± 0.02	11.2 ± 0.1	1.00	1.00
C	7.0	7.0	$(2.3 \pm 0.4) \times 10^{-3}$	0.55 ± 0.05	1.2 ± 0.01	1.15	0.17
D	7.0	10.5	$(3.3 \pm 0.3) \times 10^{-3}$	0.52 ± 0.06	11.3 ± 0.1	1.63	1.55

[a] A = absorbance at 538 nm; n_b = number of bilayers as determined by linear regression analysis. [b] t_b = thickness per bilayer as determined by ellipsometry. [c] Relative values of the slopes obtained by linear regression analysis of each series in Figure 1 and 2 relative to experiment B. [d] Too thin to measure. [e] For quartz, $\chi^{(2)} = 1.92 \times 10^{-9}$ esu.

Importantly, the pH value of the PR solutions affects the degree of ordering of the chromophore molecules in the film. When the film thickness is much less than the SHG coherence length (typically a few microns), the SHG should have a quadratic dependence on the film thickness. The linear dependence of the square root of the SHG intensity ($(I_{2\omega})^{1/2}$) on the number of bilayers for the films fabricated with a PR solution at pH 10.5 thus demonstrates there is equivalent polar ordering in each successive bilayer (Figure 2: lines B and D). When the pH value of the PR solution is held constant at 10.5, an increase in the pH value of the PAH solution from 4.5 to 7.0 results in an increase in the absorbance per bilayer (Figure 1 and Table 1, lines B and D). The value of $(I_{2\omega})^{1/2}$ per bilayer also increases by a similar relative amount and the $\chi^{(2)}$ value of the films is similar, which indicates that for these conditions the increase in SHG is simply a result of the incorporation of more PR. When the pH value of the PAH solution is held constant at 7.0 and that of the PR solution changes from 7.0 to 10.5, the bilayer thickness is similar, but the absorbance per bilayer and the $\chi^{(2)}$ value all increase. While 42 % more PR is incorporated per bilayer, the values of $(I_{2\omega})^{1/2}$ per bilayer and $\chi^{(2)}$ increase approximately eightfold. The $\chi^{(2)}$ values for films made with the PR solution at pH 10.5 are six times greater than that of quartz.

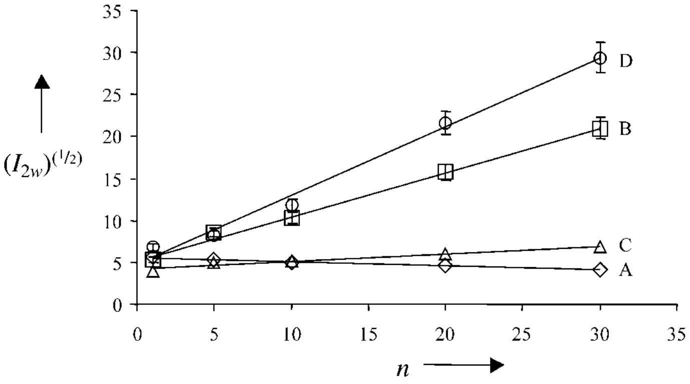

Figure 2. Square root of the SHG intensity ($(I_{2\omega})^{1/2}$) as a function of the number of bilayers for films with experimental conditions for A–D corresponding to Table 1. Lines are obtained by linear regression analysis. ◇: PAH pH 4.5/PR pH 7.0, □: PAH pH 4.5/PR pH 10.5, △: PAH pH 7.0/PR pH 7.0, ○: PAH pH 7.0/PR pH 10.5.

The dependence of the values of $\chi^{(2)}$ and $(I_{2\omega})^{1/2}$ per bilayer on the pH value of the PR solution indicates that the mechanism of PR deposition has a dramatic effect on the orientation of the PR molecules in the film. For the films made with a PR solution at pH 7.0 (experiments A and C), there is a much weaker dependence of the SHG intensity on the number of bilayers and a much lower $\chi^{(2)}$ value, which indicates a lower degree of molecular ordering of the PR molecules. At pH 7, the reactivity of the PAH amine groups with the triazine ring of the PR is lower, and PR may be incorporated by a combination of electrostatic, hydrogen-bonding, and covalent interactions. Thus at conditions favoring a covalent reaction between PR and PAH, a high degree of ordering of the PR molecules results, while under unfavorable conditions, the PR deposited within the films has a more random orientation.

We interpret the larger $\chi^{(2)}$ value and SHG observed in the deposition of PR at pH 10.5 as confirmation of our hypothesis that alternating the mechanism of deposition in these films and decoupling of the chromophore from steric constraints of a polymer backbone provides a route to low-molecular-weight chromophores. In our earlier studies with polymeric dyes bearing NLO-active chromophores as charged pendant groups, films were made under deposition conditions leading to relatively thin bilayers (ca. 0.2 nm).[14] We found by measuring SHG intensity in situ during deposition that the polar ordering of an adsorbed chromophore layer is reduced by subsequent adsorption of the next polyelectrolyte monolayer.[15] Decoupling the NLO-active chromophore from a polymer chain reduces the steric constraints for ordering that are present when using a large chromophoric side group. Additionally, competing intermolecular interactions that prevent the achievement of a high net polar ordering of the chromophore within the film can be minimized by using a “bifunctional” chromophore with which the mechanism for deposition (covalent bonding) differs from the deposition of the polymeric component (electrostatic interaction).

In conclusion, we have demonstrated a new methodology for making organic LBL films with non-centrosymmetric ordering of low-molecular-weight chromophores in each bilayer. Any chromophore with dichlorotriazine and ionic moieties can potentially be used in this scheme. While the initial $\chi^{(2)}$ values are significant, they are far from optimized because Procion Red is not an ideal NLO chromophore. We are currently testing other commercially available reactive dyes and developing new triazine-functionalized NLO chromophores with larger hyperpolarizability values.

Experimental Section

PR (Aldrich) and PAH (M_W = ca. 70000, Aldrich) were used as received. Glass microscope slides (Fisher Scientific) were used as the substrates and prepared by using the RCA cleaning procedure.[16] Solutions of PAH (10 mM, based on the monomer) and solutions of PR (25 mM) in deionized water were used in all experiments. The pH values of the solutions were adjusted with HCl or NaOH. The immersion time in PAH was 5 min, with the exception of the first layer, which was immersed for 10 min. The immersion time in PR was 10 min. The substrates were rinsed thoroughly with deionized water between immersions. The slides were dried after every ten bilayers with N_2. For each set of conditions, a series of five slides was made with a total of 2, 10, 20, 40, and 60 bilayers (counting both sides).

Absorbance and SHG measurements took into account the films deposited on both sides of the substrate, while ellipsometry measurements were made with films deposited on only one side. Absorption measurements were made with a Hitachi U-2000 spectrophotometer at a wavelength of 538 nm and were taken every ten bilayers during the deposition process. Film thicknesses were measured with a variable-angle spectroscopic ellipsometer (J. A. Woolam Ellipsometer VB-200). Ellipsometric data were obtained from the unfrosted face of the slide, as the scattering eliminates backside reflections and simplifies data analysis. The amplitude factor (ψ) and phase factor (Δ), which are related to the complex Fresnel coefficients for any given film,[17] were measured for wavelengths from 350 to 1000 nm at 10 nm intervals. This wavelength range was repeated for angles ranging from 55 to 75° in 5° intervals.

SHG measurements were performed with a standard setup using a 10-ns pulse-width, Q-switched Nd:YAG laser with a fundamental wavelength of 1064 nm. The SHG data were averaged over 100 shots per data point, and the uncertainty in the relative $\chi^{(2)}$ values is 10%. Typical spot radius and pulse energy values were 30 μm and 7 mJ pulse^{-1}, respectively. The film was deposited on both sides of the substrate. As a result, as the sample was rotated with respect to the incident beam, the path length between the films on opposite sides was varied, which led to interference fringes of the SHG intensity. The sample was rotated from 30 to 60° away from normal incidence using a stepper-motor-controlled rotation stage. The $\chi^{(2)}$ values were determined from the peak of the interference fringe in the vicinity of 45°. By comparison to Maker fringes in a quartz crystal wedge, the $\chi^{(2)}$ value of a film was obtained from $\frac{\chi^{(2)}_{\mathrm{film}}}{\chi^{(2)}_{\mathrm{q}}} = \frac{2\,l_{\mathrm{c,q}}}{\pi l_{\mathrm{film}}}\sqrt{\frac{\mathrm{I}^{2\omega}_{\mathrm{film}}}{\mathrm{I}^{2\omega}_{\mathrm{q}}}}$ where l_{film} is the total path length through the film, the coherence length of quartz ($l_{\mathrm{c,q}} = \lambda/4(n^{2\omega} - n^{\omega})$) is 22.4 μm, and the $\chi^{(2)}$ value of quartz is 1.92×10^{-9} esu.

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