

# Hybrid Covalent/Ionic Self-Assembly of Organic Second Order Nonlinear Optical Films

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**Abstract:** Ionically self-assembled monolayer (ISAM) films have been shown to spontaneously produce noncentrosymmetric ordering that gives rise to a substantial second order nonlinear optical (NLO) response. Previously, the ISAM films for NLO response consisted of bilayers of oppositely charged polymers whose thickness can be controlled through variation of pH and ionic strength of the immersion solutions. Here, we present an approach that replaces the NLO-active polymer layers with layers of monomeric chromophores containing ionic and covalent bonding sites. We have examined the effect of the pH of the immersion solutions on the orientation of the monomeric chromophores and demonstrated bulk polar ordering with  $\chi^{(2)}$  values six times larger than quartz.

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## Introduction

The formation of ionically self-assembled monolayer (ISAM) films, grown monolayer by monolayer by alternately immersing a charged substrate in anionic and cationic polymer solutions, has proven to be an easy, fast, and inexpensive method for creating laterally homogeneous nanostructured thin films [1,2]. Upon each immersion, an exceptionally homogeneous layer is rapidly (less than one minute) adsorbed and the thickness of each monolayer can be controlled to be 0.3 to >5.0 nm by varying the pH and ionic strength of the solutions. A few groups, including ours, have been examining the use of the ISAM technique for the production of films with a second order nonlinear optical (NLO) response because of the potential for dramatically improved electro-optic devices [3-10]. These films show substantial  $\chi^{(2)}$  values with excellent temporal and thermal stability. In addition, the study of ISAM films via second harmonic generation (SHG) affords valuable insight into the film structure. Films fabricated with an NLO polymer result in significant cancellation of the chromophore orientations. This cancellation occurs by two mechanisms: competitive orientation due to the ionic bonding of the polymer chromophore with the subsequent polycation layer, and random orientation of the chromophores within the bulk of each thick polyanion layer. A reduction in film thickness accompanied by an increase in net polar ordering is one possible avenue to obtain the  $\chi^{(2)}$  necessary for efficient electro-optic devices. In this paper, we describe a hybrid covalent / ionic self-assembly technique that utilizes monomer chromophores with ionic and covalent bonding sites. This novel approach overcomes the disadvantages inherent with polymer

chromophores and yields a substantial increase in  $\chi^{(2)}$  by significantly reducing competitive chromophore orientation and random orientation.

### Experimental details

ISAM films are grown monolayer by monolayer by alternately immersing a charged substrate in anionic and cationic solutions forming a multilayer structure. The immersion process can be repeated indefinitely until a desired thickness or number of bilayers has been achieved. For the studies presented here, films were deposited on cleaned glass microscope substrates. The hybrid covalent / ionic films were produced using Procion Red MX-5B (PR, from Aldrich), which contains two sulfonic acids for ionic bonding and two potential covalent bonding sites at the chlorines of 2,4-dichloro-s-triazine. Poly(allylamine hydrochloride) (PAH), was used to provide both the nucleophilic primary amine groups for reaction with the triazine ring and the protonated amine groups for electrostatic interaction with the sulfonic acid groups of PR (Figure 1). PAH solutions at a concentration of 0.01 M on a monomer basis were used in all experiments. The concentrations of PR solutions were 0.025 M. The pH of the solutions was adjusted using HCl or NaOH as needed. The glass slide immersion time in PAH was 5 minutes, with the exception of the first layer, which was 10 minutes. The immersion time in PR was 10 minutes. Between immersions, the substrates were vigorously agitated and rinsed with deionized water. Measurements were performed with a standard SHG setup using a 10-nanosecond 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 relative  $\chi^{(2)}$  values is 10%. Typical spot radius and pulse energy values were 30 $\mu$ m and 7mJ/pulse, respectively. The film was deposited on both sides of the substrate. As a result, as the sample is rotated with respect to the incident beam, the path length between the film on opposite sides is varied, leading 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  $\chi^{(2)}$  value is determined from the peak of the interference fringe in the vicinity of 45° by comparison to Maker fringes in a quartz wedge.

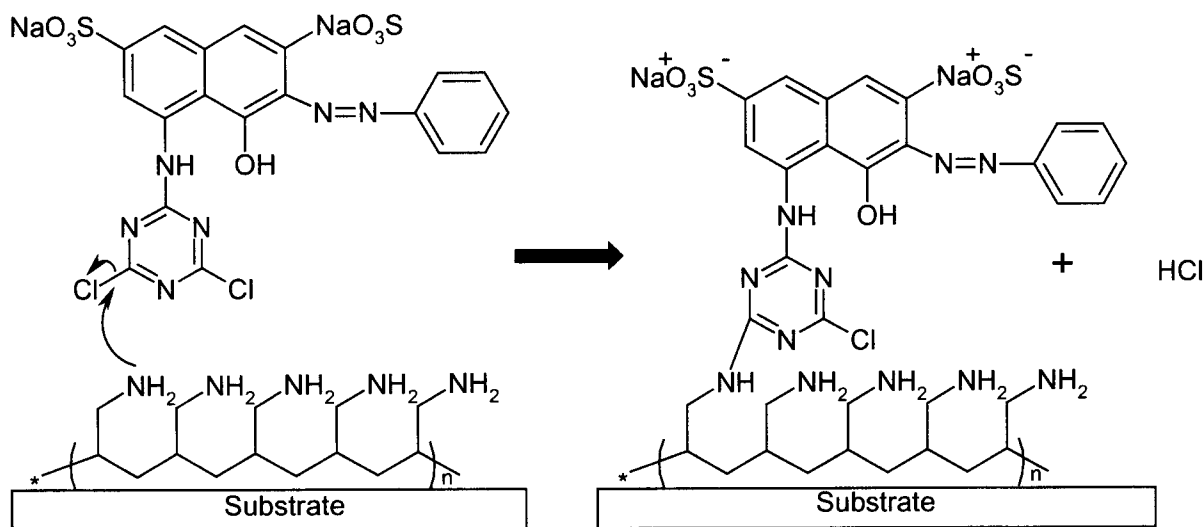


Figure 1. Reaction between PR molecule and a previously absorbed monolayer or PAH

## Results

The deposition of PR in PR/PAH films as a function of pH was monitored by absorption spectrophotometry and ellipsometry. Similar to polymeric ISAM films, these hybrid films displayed a linear increase in the absorbance as a function of the number of bilayers deposited. The slope of the absorbance as a function of number of bilayers characterizes the amount of dye deposited per bilayer; the standard deviation of this slope describes the reproducibility of the film deposition. Table 1 summarizes the absorbance slopes, bilayer thicknesses, and the  $\chi^{(2)}$  values. Successful film growth was characterized by a linear increase in the absorbance and thickness with the number of bilayers deposited and by homogeneity.

Table 1. Slopes of the absorbance vs. number of bilayers, ellipsometric thicknesses, and  $\chi^{(2)}$  for deposition of PR (0.025 M) and PAH (0.01 M RU).

PAH pH	PR pH	Slope (Abs/bilayer)	Bilayer Thickness (nm)	$\chi^{(2)}$ ( $10^{-9}$ esu)
4.5	7.0	$8.9 \times 10^{-4} \pm 1.0 \times 10^{-5}$		N/A
4.5	10.5	$2.0 \times 10^{-3} \pm 1.0 \times 10^{-4}$	$0.34 \pm 0.02$	11.2
7.0	7.0	$2.3 \times 10^{-3} \pm 4.0 \times 10^{-4}$	$0.55 \pm 0.05$	1.2
7.0	10.5	$3.3 \times 10^{-3} \pm 3.2 \times 10^{-4}$	$0.52 \pm 0.06$	11.3
10.0	10.5	$9.2 \times 10^{-3} \pm 4.6 \times 10^{-3}$	$4.3 \pm 0.3$	3.8

When the film thickness is much less than the second harmonic coherence length of the material, the SHG intensity should exhibit a quadratic dependence on the film thickness or, correspondingly, number of bilayers. Figure 2 shows the square root of the peak second harmonic intensity as a function of the number of bilayers for the sets of films fabricated with different PAH and Procion Red pH values. The linear dependence of the square root of the SHG intensity on the number of bilayers for the films fabricated with Procion Red pH 10.5 demonstrates that the SHG signal is due to polar ordering in each successive bilayer of the film. If the degree of ordering decreased in successive bilayers or if the SHG signal was due to interface effects, the SHG intensity would have a subquadratic dependence on the number of bilayers. For the films fabricated with Procion Red pH 7, the much weaker dependence of the SHG intensity on the number of bilayers is indicative of a lesser degree of ordering, as discussed below.

We have also monitored the growth of the self-assembled films in real time using *in situ* second harmonic generation. In this case, the glass substrate was held fixed in the laser beam throughout the procedure. Because the glass cuvettes, the immersion solutions, and the substrate are all centrosymmetric, the SHG signal is due to the polar film as it grows on the substrate along with a small background signal from the air-glass and glass-liquid interfaces. The substrate was first immersed in PAH solution at pH 7.0 to produce a cationic surface. Figure 3 shows the SHG intensity as a function of time as the substrate was then immersed in a PR pH 10.5 solution. The covalent deposition of Procion Red on PAH is essentially complete in two minutes.

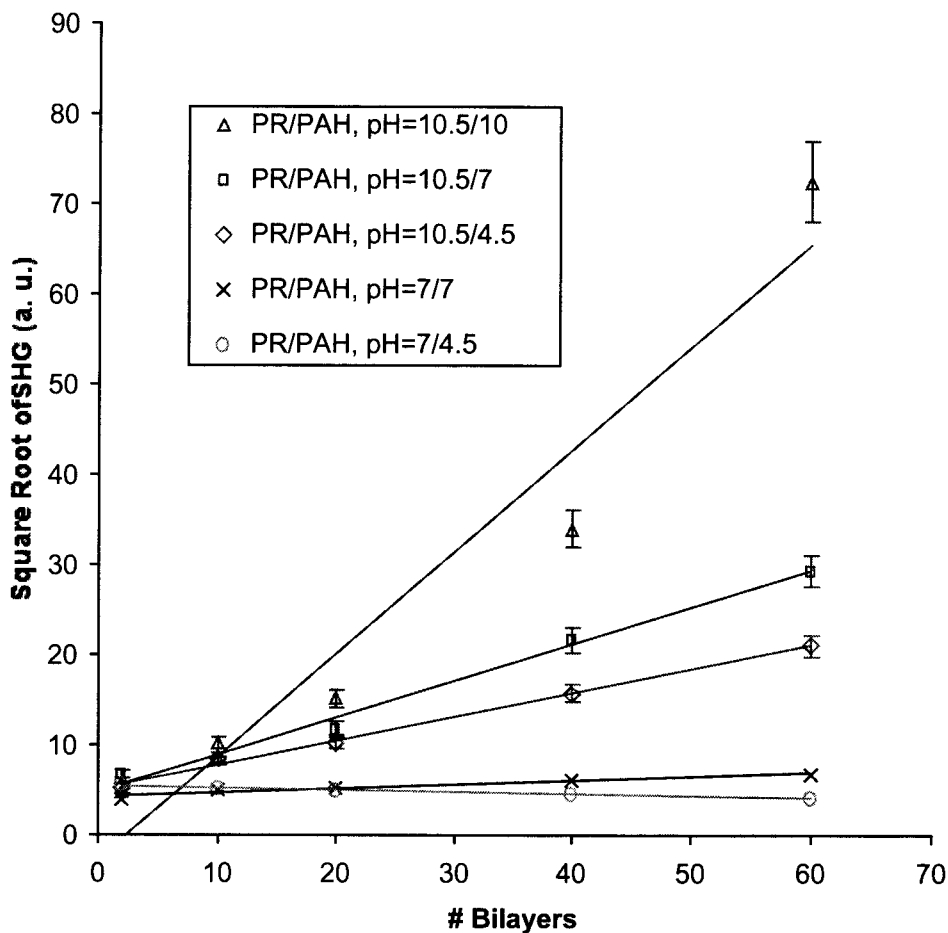


Figure 2. Square root of the SHG intensity as a function of the number of bilayer for various Procion Red/PAH pH conditions.

We have found that the pH of the polyelectrolyte and dye solutions is a key variable in this deposition process. The pH determines the ionization state of the amine side groups on PAH, which affects both the configuration of the polymer upon adsorption and its subsequent reactivity with Procion Red. Efficient electrostatic deposition of PAH requires that the pH of the PAH dipping solution is maintained near or below the amino group  $pK_a$  (8.7), where the majority of the side groups will be protonated and available for interaction with the negative charges on the substrate and the sulfonate groups on the dye. The PR solution pH directly affects the degree of protonation of the previous deposited PAH layers. At a pH above the  $pK_a$  of the side chain amines of PAH, the majority of the amines will be unprotonated and thus able to react with the triazine ring of PR. Additionally, the reactivity of the triazine ring on PR increases with increasing pH. These two effects result in reactive deposition being favored as the pH is increased.

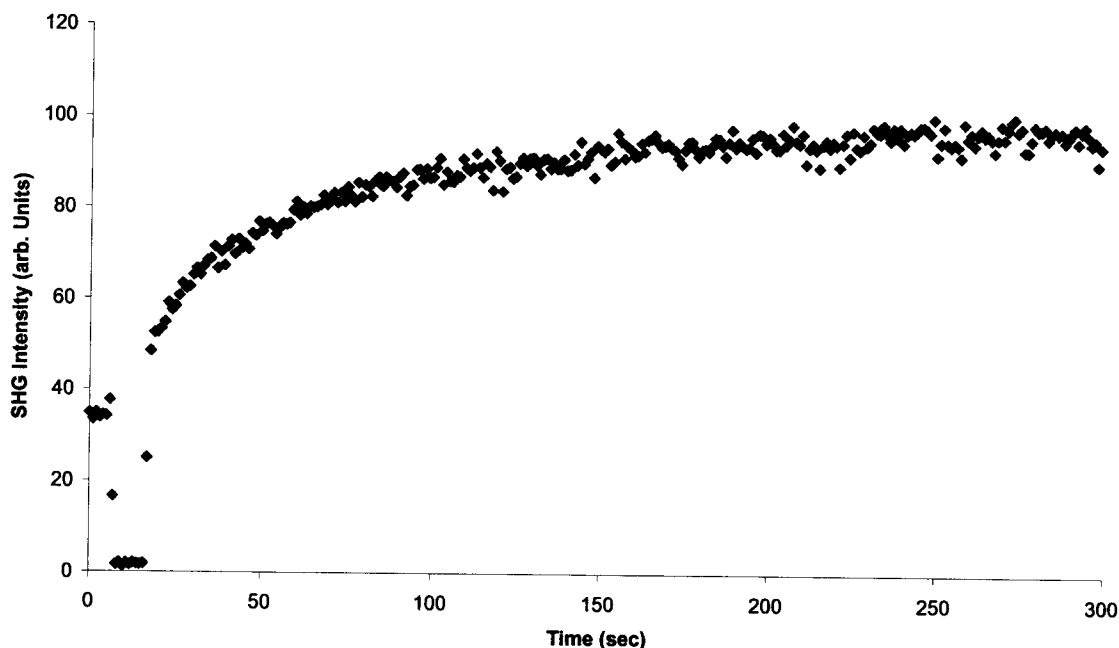


Figure 3. *In situ* measurement of the SHG intensity as Procion Red is deposited in the film. The substrate was coated with PAH (pH 7.0) and then immersed in Procion Red (0.025 M, pH 10.5).

As seen in Figure 2, the SHG observed from films deposited with Procion Red at pH 10.5 is dramatically larger than that from films deposited at pH 7.0. This is not simply a reflection of the amount of Procion Red deposited, which is directly indicated by the absorbance/bilayer column of Table I. In fact, films fabricated at PAH pH/Procion Red pH 7.0/7.0 contain a similar amount of Procion Red per bilayer as those fabricated at pH conditions 4.5/10.5. The large SHG observed in the latter case is taken as confirmation of the expected preference of covalent over electrostatic attachment of Procion Red to PAH (i.e., orientation of the triazine ring towards the PAH layer and the the sulfonates away from it.)

For the films deposited at Procion Red pH 10.5 to yield polar ordering through the predominance of covalent attachment, the absorbance per bilayer, the bilayer thickness, and the SHG intensity each increase with increased pH of the PAH solution. Increased pH of the PAH solution leads to a larger fraction of curved polymer segments and the adsorption of thicker layers. This, in turn, provides more binding sites for Procion Red deposition. The relative values of the absorbance per bilayer (indicating amount of Procion Red per bilayer), thickness per bilayer, and square root of the SHG signal per bilayer, all normalized to the values at PAH/Procion Red pH conditions 4.5/10.5 are shown in Table 2. The relative values of absorbance per bilayer and  $(I^{2\omega})^{1/2}$  per bilayer are essentially identical for films made at Procion Red pH 10.5. This indicates that the degree of chromophore orientation is the same for each case. For 7.0/10.5 pH films, the thickness per bilayer also increases in the same proportion relative to 4.5/10.5 films, showing that the PAH and Procion Red thicknesses per bilayer increase by the same amount. For the pH 10.0/10.5 films, the thickness per bilayer increases by a factor of three more than the absorbance per bilayer, indicating that these films consist of a much larger fraction of PAH relative to Procion Red. It is due to this larger fraction of NLO-inactive material that the  $\chi^{(2)}$  value of the pH 10.0/10.5 films is smaller than those of the pH 4.5/10.5 and 7.0/10.5 films.

Table 2 - Relative values of the absorbance, thickness, and  $(I^{2\omega})^{1/2}$  per bilayer as a function of deposition pH, all normalized to the values for PAH at pH 4.5 and Procion Red at pH 10.5.

PAH pH	Procion Red pH	Absorbance/bilayer	Thickness/bilayer	$(I^{2\omega})^{1/2}$ /bilayer
4.5	10.5	1.0	1.0	1.0
7.0	10.5	1.63	1.53	1.55
10.0	10.5	4.60	12.6	4.31
7.0	7.0	1.15	1.61	0.17

## Conclusions

We have demonstrated that a hybrid covalent/ionic deposition scheme can be used to obtain highly ordered self-assembled films. We propose that the ordering is induced by alternating the mechanism of deposition from monolayer to monolayer and decoupling the chromophore from the steric constraints of a polymer backbone. Using Procion Red MX-5B as a model reactive/anionic monomeric NLO chromophore and PAH as the cationic polyelectrolyte, films with significant  $\chi^{(2)}$  values were fabricated. This deposition process is highly sensitive to the pH values of both the PAH and PR solutions. In this work, we focused on the effect of pH on the film properties, and we found conditions for optimal deposition and orientation. The PR solution pH should be high enough to favor covalent deposition. The PAH solution pH should also be as high as possible while still obtaining layer-by-layer growth of homogeneous films. While the initial  $\chi^{(2)}$  values are reasonably large, they are far from optimized because the Procion Red chromophore is far from an ideal NLO chromophore. We are currently developing a triazine functionalized NLO chromophore with a higher hyperpolarizability value than Procion Red.

## Acknowledgements

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