Efficient, Thermally Stable, Second Order Nonlinear Optical Response in Organic Hybrid Covalent/Ionic Self-Assembled Films

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Efficient, Thermally Stable, Second Order Nonlinear Optical Response in Organic Hybrid Covalent/Ionic Self-Assembled Films

Abstract

A covalent/electrostatic layer-by-layer self-assembly method was used to achieve polar ordering of a water soluble, reactive dye in the fabrication of nonlinear optical (NLO) films. We observed a quadratic relationship between the second harmonic intensity $I_{2\omega}$ and bilayer number for all films made with Procion Brown MX-GRN, demonstrating that the polar ordering of the chromophores is consistent in each successive bilayer. As the ionic strength of the dye deposition solution was increased to 0.5 M NaCl, the $\chi^{(2)}_{zzz}$ of the films increased by approximately 250% to $50 \times 10^{-9}$ esu, with a corresponding average chromophore tilt angle of $38^\circ$. This was attributed to increase shielding of the dye charges which led to higher chromophore density in the bilayers. The electrooptic coefficient for films of 50 bilayers fabricated at 0.5 M NaCl was $14 \pm 2$ pm/V. Importantly, these films exhibited excellent thermal stability, with only a 10% decrease in $(I_{2\omega})^{1/2}$ after 36 h at 85 °C and then 24 h at 150 °C. Furthermore, the $(I_{2\omega})^{1/2}$ recovered completely upon cooling to room temperature. These results with a commodity textile dye point to the potential value of this class of reactive chromophores and this self-assembly method for fabrication of electrooptic materials at ambient conditions from aqueous solutions.

Comment: This paper was originally published in the Journal of “Langmuir” Volume 22. and Issue No.11, May 27 2006 Pages 5723-5727. All the copy rights © of this paper belongs to American Chemical Society.
Figure 1. (A) Procion Red MX-5B (1). (B) Covalent deposition of Procion Brown MX-GRN (2) onto an adsorbed layer of poly-(allylamine hydrochloride) (3).

Figure 2. Second harmonic intensity as a function of incident angle for Procion Brown/PAH films consisting of 20 (●), 40 (■), and 60 (▲) bilayers made at [NaCl] = 0.5 M. The shifts in angular position of the peaks is due to differences in substrate thickness.
Figure 3. Square root of the second harmonic intensity $[(\frac{I_2}{I_0})^{1/2}]$ as a function of the number of bilayers deposited for various NaCl concentrations: $\bullet = 1.0 \text{ M} ; \square = 0.5 \text{ M} ; \Diamond = 0.25 \text{ M} ; \bigcirc = 0.1 \text{ M} ; \triangle = \text{no added NaCl.}$

<table>
<thead>
<tr>
<th>[NaCl] (M)</th>
<th>bilayer thickness (nm)</th>
<th>absorbance/bilayer ($\times 10^{-1}$) (^a)</th>
<th>absorbance/nm ($\times 10^{-1}$) (^b)</th>
<th>$\langle \psi \rangle$ (degrees)</th>
<th>$\chi_{22}^{(2)} (10^{-2} \text{ em})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.27 ± 0.01</td>
<td>1.0 ($R^2 = 0.94$)</td>
<td>3.7</td>
<td>43 ± 2</td>
<td>20 ± 2</td>
</tr>
<tr>
<td>0.10</td>
<td>0.32 ± 0.01</td>
<td>1.4 ($R^2 = 0.97$)</td>
<td>4.4</td>
<td>41 ± 2</td>
<td>28 ± 2</td>
</tr>
<tr>
<td>0.25</td>
<td>0.42 ± 0.02</td>
<td>2.2 ($R^2 = 0.99$)</td>
<td>5.2</td>
<td>39 ± 2</td>
<td>49 ± 2</td>
</tr>
<tr>
<td>0.50</td>
<td>0.57 ± 0.03</td>
<td>2.9 ($R^2 = 0.99$)</td>
<td>5.1</td>
<td>38 ± 2</td>
<td>50 ± 2</td>
</tr>
<tr>
<td>1.00</td>
<td>0.71 ± 0.03</td>
<td>4.0 ($R^2 = 0.99$)</td>
<td>5.6</td>
<td>39 ± 2</td>
<td>42 ± 2</td>
</tr>
</tbody>
</table>

\(^a\) Calculated from slopes determined from linear regression of absorbance vs bilayer number data; $R^2$ values for each are reported. \(^b\) Calculated from $(\text{abs/bilayer})/(\text{bilayer thickness})$
Figure 4. Square root of the SHG intensity (left axis, ●, normalized to 1.0 at the beginning of the experiment) of a Procion Brown/PAH film as a function of time and temperature (right axis, —) during a heating cycle.