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

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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 $\chi_{zzz}^{(2)}$ of the films increased by approximately 250% to 50 × 10^{-9} esu, with a corresponding average chromophore tilt angle of 38°. 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 ± 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.

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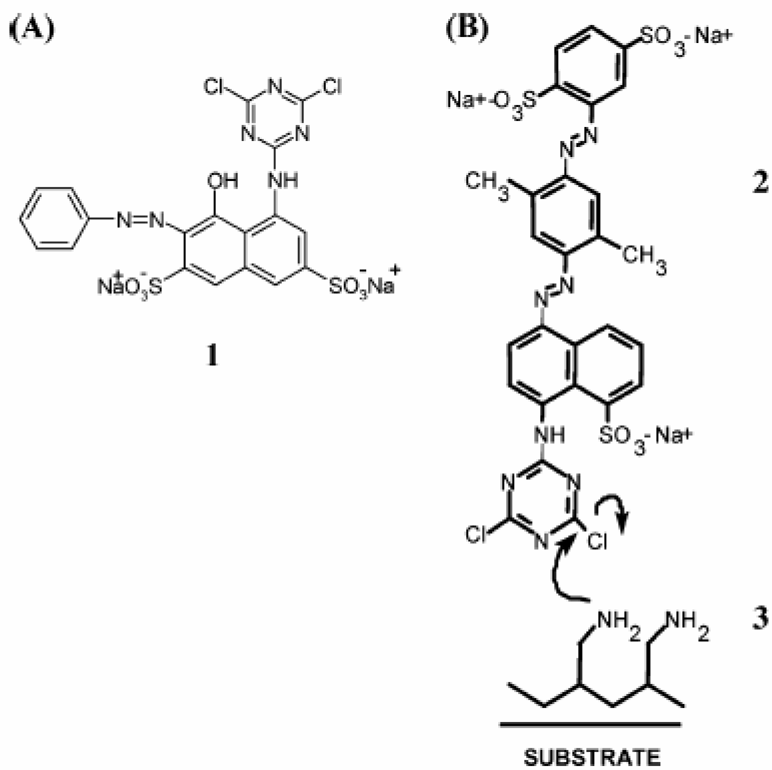

Figure 1. (A) Procion Red MX-5B (**1**). (B) Covalent deposition of Procion Brown MX-GRN (**2**) onto an adsorbed layer of poly-(allylamine hydrochloride) (**3**).

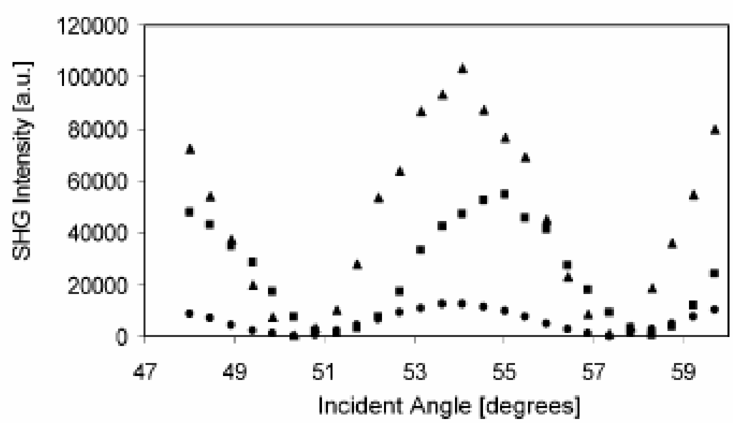

Figure 2. Second harmonic intensity as a function of incident angle for Procion Brown/PAH films consisting of 20 (●), 40 (■), and 60 (▲) bilayers made at [NaCl] = 0.5 M. The shifts in angular position of the peaks is due to differences in substrate thickness.

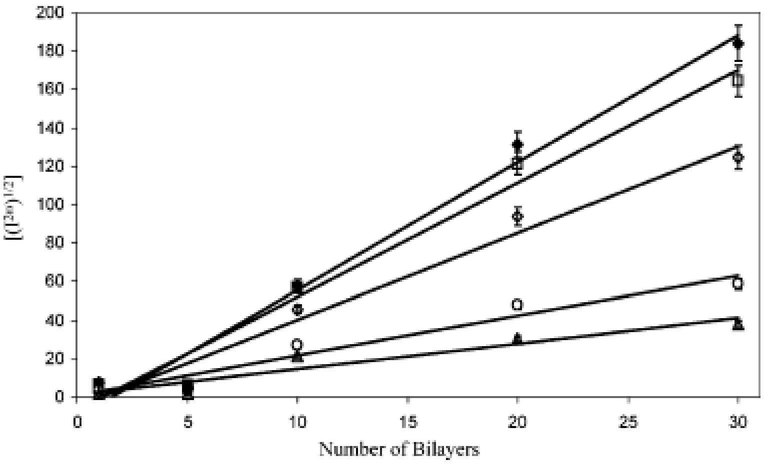

Figure 3. Square root of the second harmonic intensity $[(I^{2\omega})^{1/2}]$ as a function of the number of bilayers deposited for various NaCl concentrations: ♦ = 1.0 M; □ = 0.5 M; ◊ = 0.25 M; ○ = 0.1 M; △ = no added NaCl.

Table 1. Procion Brown MX-GRN Film Properties as a Function of NaCl Concentration in the Deposition Solutions

[NaCl] (M)	bilayer thickness (nm)	absorbance/bilayer ($\times 10^{-3}$)[a]	absorbance/nm ($\times 10^{-3}$)[b]	$\langle\psi\rangle$ (degrees)	$\chi^{(2)}_{zzz}$ (10^{-9} esu)
0	0.27 ± 0.01	1.0 ($R^2 = 0.94$)	3.7	43 ± 2	20 ± 2
0.10	0.32 ± 0.01	1.4 ($R^2 = 0.97$)	4.4	41 ± 2	28 ± 2
0.25	0.42 ± 0.02	2.2 ($R^2 = 0.99$)	5.2	39 ± 2	49 ± 2
0.50	0.57 ± 0.03	2.9 ($R^2 = 0.99$)	5.1	38 ± 2	50 ± 2
1.00	0.71 ± 0.03	4.0 ($R^2 = 0.99$)	5.6	39 ± 2	42 ± 2

[a] Calculated from slopes determined from linear regression of absorbance vs bilayer number data; R^2 values for each are reported. [b] Calculated from (abs/bilayer)/(bilayer thickness)

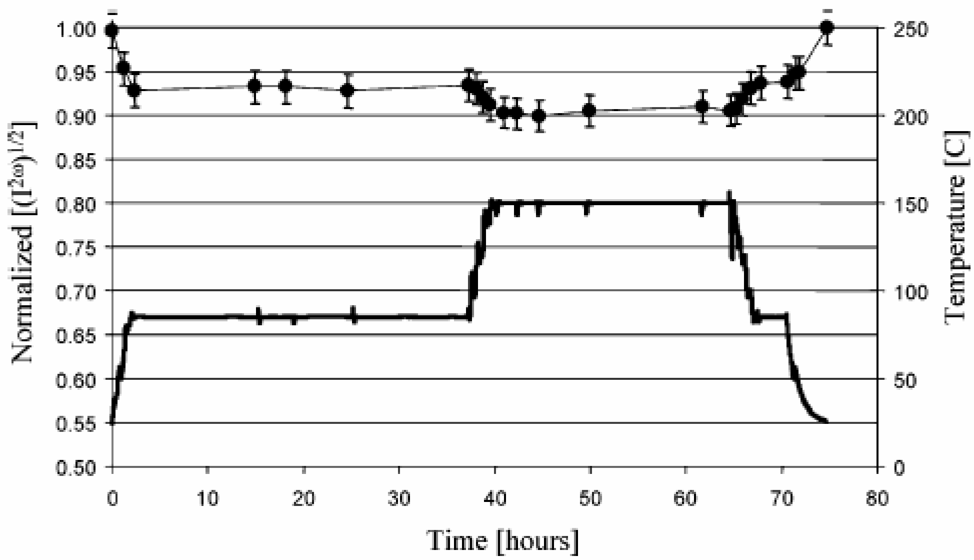

Figure 4. Square root of the SHG intensity (left axis, ●, normalized to 1.0 at the beginning of the experiment) of a Procion Brown/PAH film as a function of time and temperature (right axis, —) during a heating cycle.