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# Communications to the Editor

## Orientation of Nonlinear Optical Active Dyes in Electrostatically Self-Assembled Polymer Films Containing Cyclodextrins

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**Introduction.** Alternating polyelectrolyte adsorption is a recent, simple, and versatile method to self-assemble thin polymer films (electrostatic self-assembly, "ESA").[1,2] Assemblies have been built from various charged synthetic and natural polymers, dyes, and colloids. Typically, these films are amorphous and often described as "fuzzy",[1] as the polyelectrolyte chains are interdigitated, resulting from the film-forming mechanism.[1,2] However, for certain applications, an internal structure in the films would be desirable. Internal structure may concern the formation of well-defined sublayers,[2] but also the alignment or even the orientation of functional fragments in the films. The latter seems to be the most difficult to achieve, as film growth results from electrostatic interactions which a priori are not directed.

Second-order nonlinear optical (NLO) effects require a noncentrosymmetric orientation of the chromophores.[3] Therefore, NLO-active chromophores allow to study the orientation of such dye fragments in films by measuring second harmonic generation (SHG). In fact, NLO activity has been reported occasionally for dye functionalized ESA films.[4,5] However, the SHG signals do not increase quadratically, but level off or even decrease upon film growth due to the dynamic nature of ESA films.[4] The limited chromophore orientation is attributed to an induction by the support.[4] Only exceptionally, orientation could be maintained over a larger number of deposition cycles, leading to a quadratic increase of rather weak SHG signals with film growth.[6]

To favor chromophore orientation in ESA films, we tried to combine electrostatic self-assembly with supramolecular chemistry, namely by using inclusion complexes of a polymeric NLO active dye and a $\beta$-cyclodextrin.

**Experimental Section.** Films were deposited on glass slides by dipping them alternatively in aqueous solutions of the cation and the polyanion (concentrations $10^{-2}$ M with respect to the charges) for 20 min. The chitosane solution was adjusted to pH 2−3 with HCl. The cleaning and deposition procedures, the UV−vis equipment, and SHG setup (1064 nm fundamental beam) are described elsewhere.[4,7]

Modified $\beta$-cyclodextrin **1** was prepared by alkylation of heptakis(6-deoxy-6-iodo-$\beta$-cyclodextrin)[8] with excess pyridine. Copolymer **3** was obtained by free radical copolymerization of *N*,*N*-diallylaniline with sodium 2-acrylamido-2-methylpropanesulfonate followed by an azo coupling to the polymer. Chitosane **4** (80% deacetylated) was a gift of Wolf Walsrode AG (Germany).

**Results and Discussion.** The $\beta$-cyclodextrin ($\beta$-CDPyr **1**) bears pyridinium groups at the C-6 position of the repeat units (Scheme 1a), i.e., at one side only of the rigid cone. In relation to previous studies,[9] we envisaged that this side would preferentially adsorb to a negatively charged substrate, thus orienting (at least on average) the hydrophobic cavity of $\beta$-CDPyr **1** which can accommodate a dye (Figure 1). Oligocation **1** was compared with a linear homologous polyamine, chitosane **4**, which is extensively protonated at pH 2−3.

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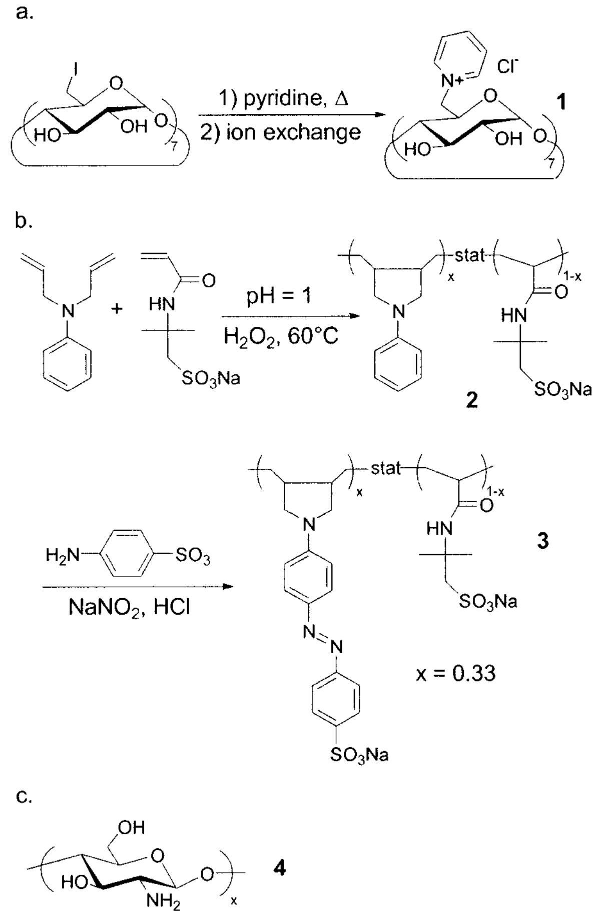
**Scheme 1. Outline of the Syntheses of 1 and 3 and Structure of 4**



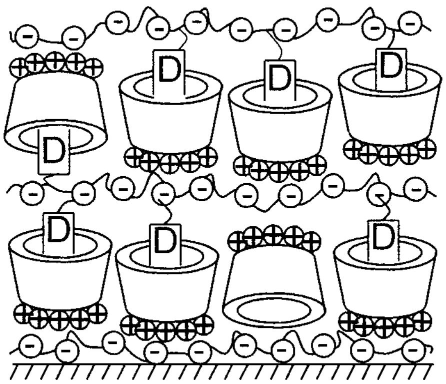


**Figure 1.** Model of induced orientation of dye fragments by charged $\beta$-cyclodextrins.

As a functional polyanion, we synthesized a copolymer bearing an azo dye (Scheme 1b, **3**). The anchoring of the chromophore to the polymer and the charge on the dye were aimed at orienting and enhancing its inclusion in the cavity of **1** at the film's interface. If the average orientation of the dye fragments remains constant for each deposition cycle, the SHG signal should grow quadratically.

Deposition of the polyion pairs {**1**/**3**} and {**4**/**3**} was monitored by UV/vis spectroscopy. The inset in Figure 2 demonstrates linear film growth. The change in slope for the pair {**4**/**3**} after 11 deposition cycles is typical for the storage of the sample in air overnight.[10] Whereas the absorbance spectra of films $\{\mathbf{4}/\mathbf{3}\}_{20}$ grown with chitosane exhibit a broad shoulder indicating aggregation of the dye, this phenomenon is absent for the films $\{\mathbf{1}/\mathbf{3}\}_{20}$ grown with $\beta$-CDPyr (Figure 2). In fact, UV/vis spectra of polymer **3** in pure aqueous solution correspond to the spectra of films {**4**/**3**}. Titration of this solution with $\beta$-CDPyr **3** induces changes in the spectra until a 1:1 stoichiometry of **1**/**3** is reached. The final spectrum is virtually identical to that of a {**1**/**3**} film. These observations suggest the formation of an inclusion complex of the dye with the cyclodextrin, thus isolating the chromophores.

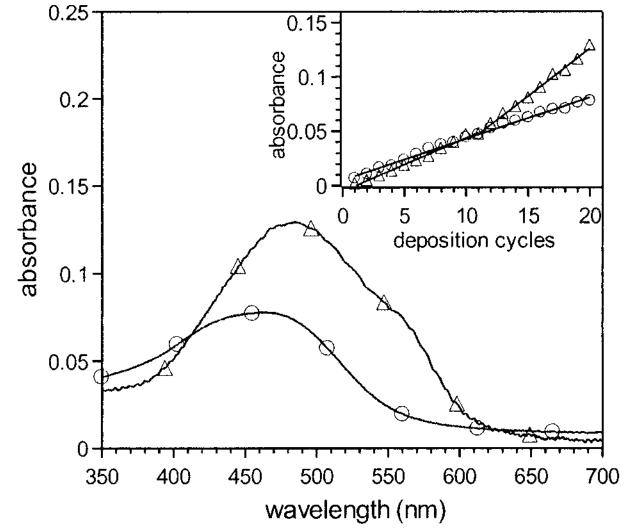


**Figure 2.** Absorbance spectra of a $\{\mathbf{1}/\mathbf{3}\}_{20}$ (○) and a $\{\mathbf{4}/\mathbf{3}\}_{20}$ film (△). The inset shows the growth of {**1**/**3**} (○) and {**4**/**3**} (△) films as followed by UV/vis spectroscopy (values taken at $\lambda_{max}$).

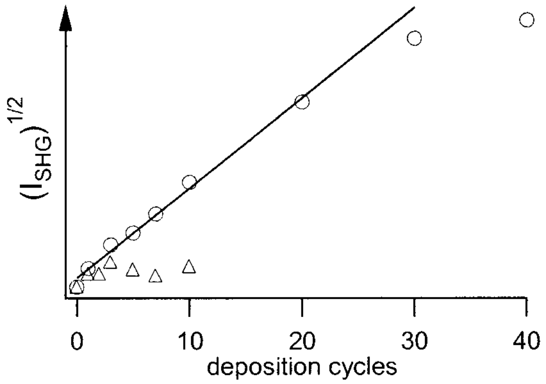


**Figure 3.** Square root of the SHG signal (arbitrary units) vs the number of deposition cycles for cyclodextrin (○) and chitosane (△) containing films.

Multilayers {**4**/**3**} containing the linear polycation exhibit increased SHG signals for the first three deposition cycles only, whereafter the signal levels off (Figure 3). This is expected for a surface-induced orientation of the dye.[4] In contrast, the square root of the SHG signal for the pair {**1**/**3**} containing the cyclodextrin increases approximately linearly with film growth for the first 10−20 deposition cycles (Figure 3). The SHG signal continues to grow for thicker films, though no longer quadratically.

Since ESA films are made under kinetic control, heating often causes a loss of orientation.[6a] Heating the {**4**/**3**} films to 100 °C gave a loss of signal of ca. 50%, which recovered to about 75% of the original value upon cooling. The {**1**/**3**} films showed a loss of only 20% upon heating. After cooling to ambient temperature, 90% of the SHG signal was recovered. This indicates that the orientation of the dyes is well stabilized in the cyclodextrin films.

The films are optically isotropic in the film plane. The values of the three, accordingly independent second-order susceptibility components, $\chi_{zzz}$, $\chi_{zxx}$, and $\chi_{xxz}$ were estimated by a recently developed polarization technique[11] and calibrated by quartz,[12] giving $\chi_{zzz} = 114$ pm/V, $\chi_{zxx} = 22$ pm/V, and $\chi_{xxz} = 41$ pm/V for sample $\{\mathbf{1}/\mathbf{3}\}_{10}$. These high values are mainly due to resonance enhancement ($\lambda_{\mathrm{SHG}} = 523$ nm). The relative values of $\chi_{zzz}$, $\chi_{zxx}$, and $\chi_{xxz}$ indicate the preferential orientation of the chromophore perpendicular to the surface. The orientation is not perfect though, since the values of $\chi_{zxx}$ and $\chi_{xxz}$ are substantial.

Though not being perfect yet, the approach demonstrates that the superposition of concepts of supramolecular chemistry and electrostatic self-assembly allows to achieve oriented structures where a simple self-organization process alone is not sufficient. The cyclodextrin entity seems to orient partially the chromophores and to prevent their reorientation, which is attributed to an inclusion complex formed. With similar concepts, the convenient, though normally structurally limited ESA method will be much enriched and will allow to prepare more complex structures.

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**Supporting Information Available:** Details of the syntheses and $^1$H NMR and IR spectra of cyclodextrin **1** and polymers **2** and **3**. This information is available free of charge via the Internet at http://pubs.acs.org.

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