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Short communication

Electrostatic layer-by-layer self-assembly of anionic squarylium and cationic polyelectrolyte

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Abstract

Alternating thin films of the anionic squarylium (SQ) dye and poly(diallyldimethylammonium chloride) (PDDA) were formed by the sequential deposition of SQ and PDDA from aqueous solution onto a glass substrate. UV–vis absorbance measurements reveal that the bilayer deposition process was linear and highly reproducible from layer to layer.

Keywords: Layer-by-layer; Self-assembly; Squarylium dye; Multilayer; Poly(diallyldimethylammonium chloride)

There has been a great interest in molecularly organized ultrathin films prepared by alternate electrostatic layer-by-layer (LBL) adsorption or electrostatic self-assembly of linear polyions [1]. Alternate adsorption of a polycation and a polyanion is readily achieved by excessive adsorption of polyelectrolytes on oppositely charged surfaces.

LBL method developed by Decher et al. has also proved to be a simple and effective technique for fabricating ultrathin organic multilayer films. This technique provides a way to control the construction of ultrathin films at nanoscale and a long-term stability of the film can be obtained easily. This approach has been extended to various other materials, including inorganic nanoparticles [2–4], dyes [5–8] and biological macromolecules such as DNA [9,10] and proteins [11,12]. SQ dyes and their derivatives are 1,3-disubstituted compounds synthesized from squaric acid and two electron-donating aromatic or heterocyclic methylene bases.

These cyanine dyes have attracted much attention because of their potential application as xerographic organic photoreceptors [13], optical recording media [14] and organic solar cells [15]. They exhibit several beneficial properties, such as photoconductivity and a sharp and intense absorption in the visible or near-infrared region [16]. We have previously reported the synthetic [17], electrochromic [18], electroluminescent [19] and electrophotographic [20] properties of symmetrical and unsymmetrical SQ dyes.

In this study, we have examined the alternate multilayer adsorption of charged SQ dye molecule with polycation. The low molecular weight chromophoric SQ dye was chosen to have sufficient charge density to allow charge compensation for the adsorption of polycation. The polyelectrolyte used for the preparation of the self-assembled film was poly(diallyldimethylammonium chloride) (PDDA), Mw 200,000–350,000. All were obtained from Aldrich Chemical Co. Milli-Q-Water was used for all cleaning steps and as the solvent for the

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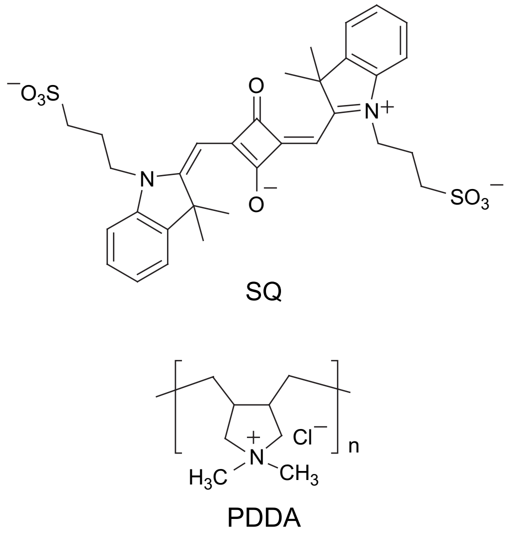

Fig. 1. Chemical structure of SQ and PDDA.

adsorption. SQ dye was synthesized by the reaction of squaric acid with the 1-δ-sulfopropyl-2,3,3-trimethyl-indolenine according to a procedure described previously [21,22]. The chemical structure of PDDA and SQ dye is shown in Fig. 1.

The glass slides (20 × 10 × 1 mm) were used as substrates for UV–vis spectroscopy. The surface of the glass is pretreated to render a net negative surface charge by placing it in 2% KOH aqueous solution under sonication for 1 h. A negatively charged glass slide was first immersed into PDDA (0.15 g/75 ml Milli-Q-water) aqueous solution for 10 min. After rinsing three times in Milli-Q-water, the modified substrate was dried with gentle stream of nitrogen. The layered support is then transferred into 10^{-4} M of SQ aqueous solution. This process is repeated until the desired number of bilayers of PDDA/SQ is obtained. All adsorption procedures were carried out at room temperature. For the self-assembly experiments, the water soluble SQ derivative was used.

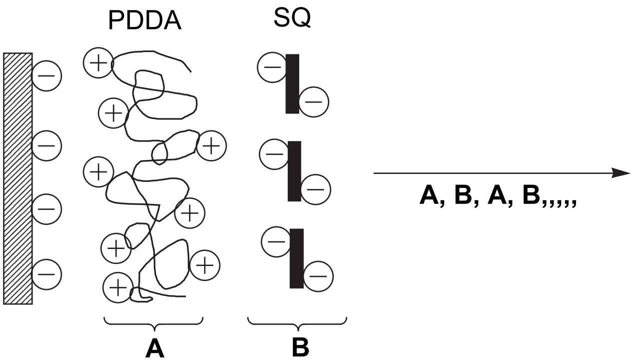

Fig. 2. Schematic view of a self-assembled alternating multilayer film composed of a cationic polyelectrolyte PDDA and an anionic SQ.

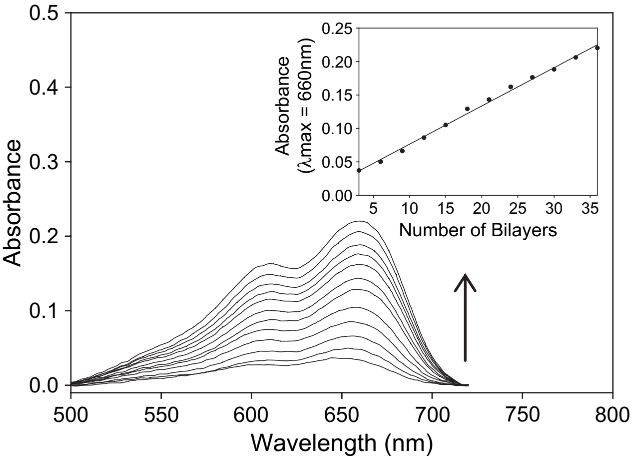

Fig. 3. UV–vis absorption spectra of PDDA/SQ multilayer films through a consecutive LBL deposition. The insert shows the increase in absorbance at 660 nm as a function of deposition cycles.

Fig. 2 shows a schematic illustration of a self-assembled film fabricated with alternating layers of two compounds.

In step A, a substrate with a negatively charged surface is immersed in the solution of the positively charged PDDA. In step B, the substrate is dipped into the solution containing the negatively charged SQ. The growth of PDDA/SQ multilayer films formed by the sequential adsorption of PDDA and SQ was examined by using UV–vis spectroscopy. In Fig. 3, the adsorption spectra of a self-assembled multilayer containing SQ and PDDA are shown.

The regularity of the LBL adsorption is demonstrated in the plot of the absorbance of SQ in its maximum at $\lambda = 660$ nm versus the number of dipping cycles applied. The SQ adsorption is clearly identified by the characteristic peaks between 500 and 700 nm. A broad spectrum with adsorption maxima at 660 nm and a shoulder at 610 and 540 nm can be seen. SQ exhibits an intense and narrow absorption peak at around 540–630 nm in chloroform. It is well known that the λ_{max} of the dyes in the solid shift to longer wavelengths compared with those in solution because of the stronger molecular interactions of dye molecules in the solid state.

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