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Self-assembly multilayer of photochromic bolaform spiroxazine

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Abstract

A novel, bolaform spiroxazine in which the hydrophobic chain comprised a hexamethylene unit and a 1,4-diazabicyclo[2,2,2]octane unit was synthesized. Alternate multilayer films of the spiroxazine and polystyrenesulfonate (PSS) were prepared using layer-by-layer deposition. UV–vis absorbance measurements revealed that the bilayer deposition process was linear and highly reproducible. The photoinduced ionic conductivity response of the SO/PSS multilayer was also studied.

Keywords: Layer-by-layer deposition; Self-assembly; Spiroxazine; Photochromism

1. Introduction

The preparation of thin organic films has received considerable attention due to their potential application in molecular- and nano-scale devices [1,2]. The films are commonly formed using Langmuir–Blodgett (LB) deposition, controlled spin casting, vapour deposition or self-assembly techniques based on chemisorption. More recently, however, there has been great interest in molecularly organized, ultrathin films prepared by the alternate, layer-by-layer (LBL) adsorption of linear polyions or the so-called electrostatic self-assembly [3]. The LBL method developed by Decher et al. has also been shown to be a simple and effective technique for fabricating ultrathin, organic multilayer films [4,5] in which process, the substrate is dipped in two different solutions alternatively with intermediate wash-off; the overall thickness of the assembly can be controlled simply by the number of deposition cycles. This particular approach has been extended to various other materials, including inorganic nanoparticles [6–8], dyes [9–11], biological macromolecules such as DNA [12,13], proteins [14,15] and fluorescence sensors [16,17].

Photochromic materials have gained much attention recently because of their tremendous importance in biological phenomena as well as their potential application in the area of linear and nonlinear optics [18]. Structurally, spiroxazines consist of two *pi* systems linked by a tetrahedral, spiro carbon. Upon UV irradiation, the C–O bond of the colourless spiroxazine is cleaved and the coloured merocyanine form is obtained. Thus, the interconversion of the spiro (SP)–merocyanine (MC) system has been extensively investigated due to its potential application in molecular devices and in biotechnology [19]. We have previously reported the synthesis and electrostatic layer-by-layer, self-assembly of various dyes [20,21]. This paper concerns the synthesis of a novel, bolaform spiroxazine (SO) in which the hydrophobic chain comprises a hexamethylene unit and a diammonium of 1,4-diazabicyclo[2,2,2]octane unit. The LBL multilayer fabrication and characterization of the newly synthesized bolaform SO are also described.

2. Experimental

2.1. Materials and measurement

1,3,3-Trimethyl-2-methyleneindolin, 1-nitroso-2,7-dihydroxynaphthalene, 1,6-dibromohexane, 1,4-diazabicyclo[2,2,2]octane

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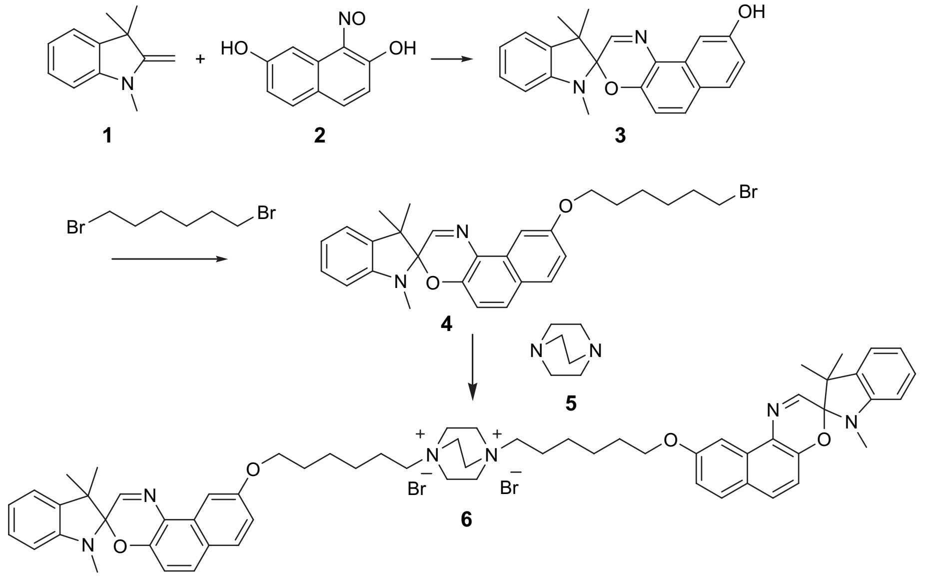


Scheme 1. Synthesis of bolaform spiroxazine (SO), **6**.

and polystyrenesulfonate B (sodium salt, $M_r = 70{,}000$) (PSS) were purchased from Aldrich. The analytical grade solvents were dried with an appropriate drying agent and distilled prior to use. Milli-Q water was used as the solvent in preparing the polyelectrolyte solutions for LBL deposition of SO and PSS. Melting points were determined using an Electrothermal IA 900 and are uncorrected. A multichannel photodiode detector (MCPD, Otsuka Electronics, Co., Japan) was used to obtain visible absorption spectra and CHN analyses were carried out with a Carlo Elba model 1106 analyzer. ^{1}H NMR spectra were recorded on a Varian Unity Inova 400 MHz FT-NMR spectrometer with TMS as internal standard. Atomic force microscopy (AFM) of the sample surface morphology in air was conducted using a Nanoscope IV Multimode; photographic images were recorded in the conventional height mode (tapping mode, normal AFM). For the measurement of photoinduced ionic conductivity, the device comprised two ITO glasses (3 × 3 cm) separated by a 0.1 mm thickness spacer of PET film placed so as to face each other on the inside of the cell; the edges of the cell were sealed with insulating, epoxide resin. The multilayer assemblies of SO/PSS were deposited on only one ITO glass surface. Prior to final sealing, the space between the electrodes was filled with a Milli-Q water/DMSO solution of 0.05 mmol SO and 1 mmol of tetra-*n*-butylammonium perchlorate, ($[CH_3(CH_2)_3]_4NClO_4$ – *caution*: contact with combustible material may cause fire) as electrolyte. A high pressure mercury lamp (Ushio, SP3-250D) was used as the UV radiation source and was calibrated with a monochromator at 366 nm.

2.2. Synthesis of compound 4

1,3,3-Trimethyl-6'-hydroxyspiro[2*H*]-indol-2,3'-[3*H*]-naphth[2,1-b][1,4]oxazine (**3**) was prepared from 1,3,3-trimethyl-2-methyleneindoline (**1**) and 1-nitroso-2,7-dihydroxynaphthalene (**2**) according to the method described in the literature [22,23].Yield 50%; mp 212–214 °C. Anal. Calcd for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.89; H, 4.97; N, 8.59.

A stirred solution of **3** (1 g, 2.9 mmol) and 1,6-dibromohexane (1.47 g, 2.9 mmol) in acetone (150 ml) containing powdered potassium carbonate (0.32 g) was refluxed for 24 h. The solution was filtered and the filtrate was evaporated under reduced pressure. The product obtained was washed with methanol several times and recrystallized from hexane. Yield 79%; mp 147 °C; MS *m/z* M^+ 507; ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 6H), 1.57 (s, 5H), 1.91 (m, 4H), 3.44 (t, $J = 6.52$ Hz, 2H), 4.18 (t, $J = 6.52$ Hz, 2H), 6.57 (d, $J = 8.04$ Hz, 1H), 6.84 (d, $J = 9.00$ Hz, 1H), 6.89 (t, $J = 8.04$ Hz, 1H), 7.03 (d, $J = 9.1$ Hz, 1H), 7.08 (d, $J = 6.52$ Hz, 1H), 7.20 (t, $J = 7.16$ Hz, 1H), 7.56 (d, $J = 9.04$ Hz, 1H), 7.63 (d, $J = 9.04$ Hz, 1H), 7.71 (s, 1H), 7.84 (s, 1H). Anal. Calcd for $C_{28}H_{31}N_2O_2Br$: C, 66.27; H, 6.16; N, 5.52; O, 6.31. Found: C, 66.95; H, 6.43; N, 6.07; O, 6.27.

2.3. Synthesis of 6

Compound **4** (3 g, 5.9 mmol) and 0.33 g (2.9 mmol) 1,4-diazabicyclo[2,2,2]octane (**5**) in 180 ml of acetonitrile were refluxed for 72 h. The reaction mixture was cooled to room temperature and filtered, washed with methanol and then ether

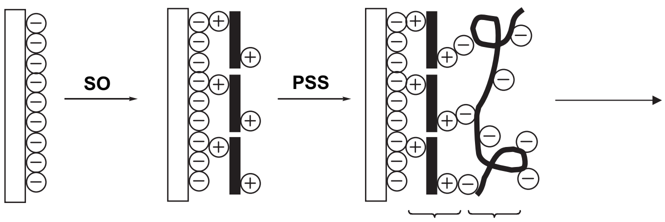


Fig. 1. Schematic representation of the adsorption process.

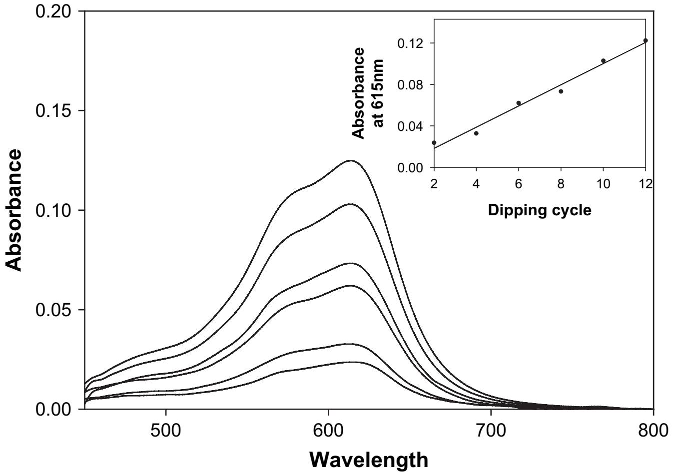


Fig. 2. UV–vis absorption spectra of SO/PSS multilayer films through a consecutive LBL deposition. The inset shows the increase in absorbance at 615 nm after UV irradiation as a function of deposition cycle.

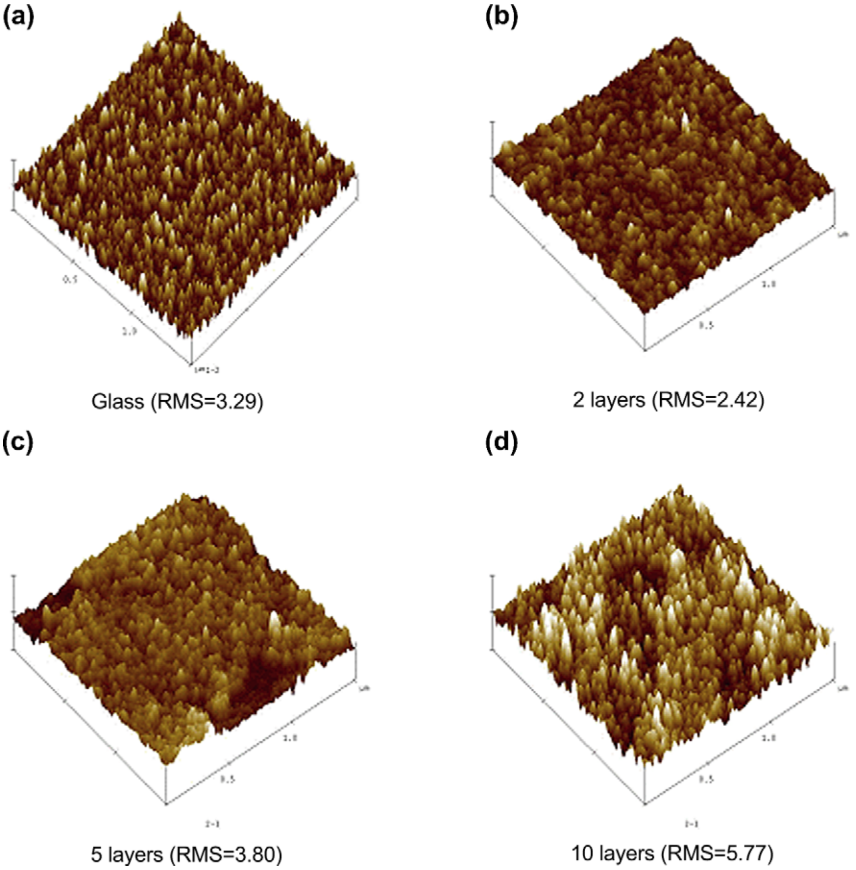
and dried. Yield 16%; mp 203 °C; ^{1}H NMR (DMSO-d_6) δ 7.83 (s, 2H), 7.81 (s, 2H), 7.76 (d, $J = 9.04$ Hz, 2H), 7.70 (d, $J = 9.04$ Hz, 2H), 7.15 (m, 4H), 7.04 (d, $J = 8.80$ Hz, 2H), 6.91 (d, $J = 9.04$ Hz, 2H), 6.83 (t, $J = 7.56$ Hz, 2H), 6.65 (d, $J = 7.52$ Hz, 2H), 4.15 (t, $J = 6.04$ Hz, 4H), 3.90 (t, 12H), 3.55 (t, $J = 8.04$ Hz, 4H), 2.69 (s, 6H), 1.85 (m, 4H), 1.77 (m, 4H), 1.56 (m, 4H), 1.41 (m, 4H), 1.28 (s, 6H), 1.25 (s, 6H).

2.4. Thin film fabrication via self-assembled, layer-by-layer deposition

A glass slide (20 × 10 × 1 mm) was used as the substrate for UV–vis spectroscopy. The surface of the glass was pretreated to render a net negative surface charge by placing it in 2% aq. KOH solution under sonication for 1 h. The ensuing negatively charged glass slide was first immersed in a solution containing 8 mg SO in a mixture of 60 ml Milli-Q water and 40 ml DMSO for 20 min. After rinsing three times with Milli-Q water, the modified substrate was dried in a gentle stream of nitrogen and then immersed in a solution containing 0.21 g PSS in 20 ml Milli-Q water. This process was repeated until the desired number of bilayers of SO/PSS was obtained. All procedures were carried out at room temperature.

3. Results and discussion

The synthetic route to SO (**6**) is outlined in Scheme 1. Compound **3** was prepared from 1,3,3-trimethyl-2-methyleneindoline (**1**) and 1-nitroso-2,7-dihydroxynaphthalene (**2**) according to the method described in the literature [22,23]. The reaction of **3** with 1,6-dibromohexane gave **4** in 79% yield; **4** was then reacted with 1,4-diazabicyclo[2,2,2]octane (**5**) in acetonitrile to yield the bolaform SO, **6**.



Glass (RMS=3.29)
2 layers (RMS=2.42)
5 layers (RMS=3.80)
10 layers (RMS=5.77)

Fig. 3. Tapping mode AFM image of SO/PSS multilayer on glass.

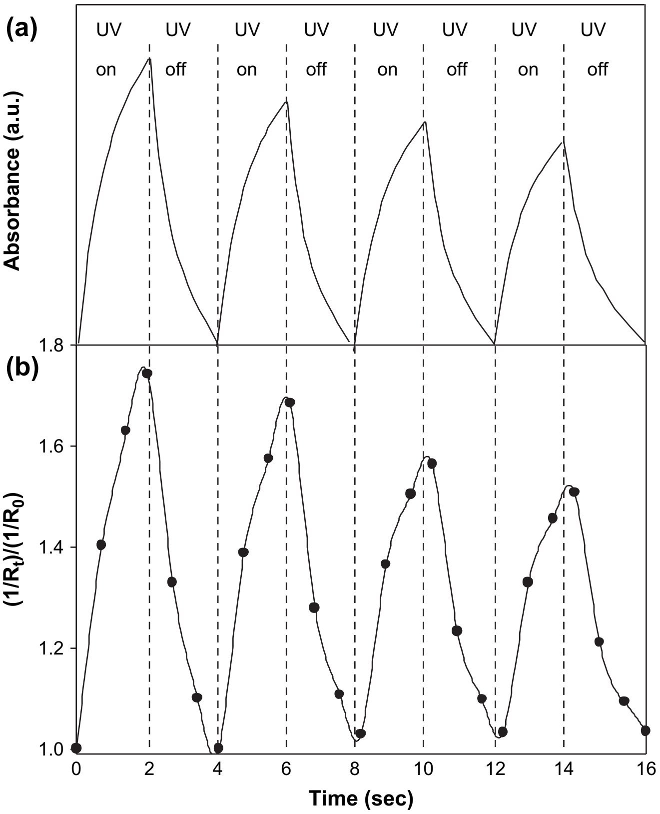


Fig. 4. Absorbance change at 615 nm (a) and photoinduced ionic conductivity response (b) following periodic UV irradiation for SO/PSS multilayer.

A proposed model of the multilayer obtained by *n* dipping cycles is given in Fig. 1. In step A, the substrate with a negative charged surface is immersed in a solution of the positively charged SO; in step B, the substrate is dipped in a solution containing the negatively charged PSS.

UV–vis spectroscopy was used to investigate both the assembly process of the dye layers and aggregation phenomena [24]. The growth of the SO/PSS multilayer film formed by the sequential adsorption of PSS and SO was examined using UV–vis spectroscopy. Fig. 2 shows the adsorption spectra of the self-assembled multilayer upon UV irradiation. The films were clear and transparent in appearance; the regularity and uniformity of the LBL adsorption are demonstrated by a plot of the absorbance of SO at its λ_{max} (615 nm) as a function of the number of dip cycles.

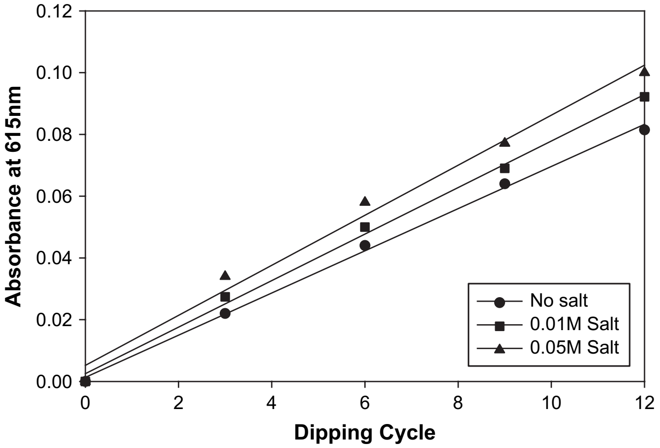


Fig. 5. Salt concentration effect on SO/PSS multilayer (measured at 615 nm after UV irradiation). The solution is adjusted to three different ionic strengths by the addition of NaCl: no salt (●); 0.01 M (■), 0.05 M (▲).

More detailed information on the surface structure of the self-assembled multilayer on the glass surface was obtained using AFM. The morphology of 0, 2, 5 and 10 layer SO/PSS films is shown in Fig. 3. The surface roughness, RMS, as inferred from the mean height measured from the cross-sectional analysis of raw glass, was about 3.29 nm; the roughness of the 2, 5, 10 layer SO/PSS multilayer was 2.42, 3.80 and 5.77 nm, respectively. These direct AFM images provide evidence of multilayer formation by stepwise chemical assembly.

Upon UV irradiation, a broad absorption band appeared at about 615 nm. When the sample was left in the dark at room temperature after irradiation, the absorbance at 610 nm decreased. The new band is ascribable to the generation of the open merocyanine form from the closed spiro form. The SO exhibited fairly good reversibility, as can be seen in Fig. 4a, where consecutive coloration–decoloration cycles are shown. The photoinduced ionic conductivity response at 15 °C (Fig. 4b) was estimated from the expression: $(1/R_t)/(1/R_0)$ where R_0 and R_t are the resistance before and after UV irradiation. Sufficient reversibility was found in the multilayer and this response was completely synchronized with that of the absorbance changes.

The effect of electrolyte on the SO/PSS multilayer was investigated by adjusting the water/DMSO dipping solution of SO to two different ionic strengths by the addition of 0.01 and 0.05 M NaCl. Fig. 5 shows the UV–vis absorbance of the multilayers at 615 nm as a function of the number of layers deposited. The results showed that high electrolyte concentrations tended to promote surface adsorption.

4. Conclusions

Alternate multilayer films of the novel bolaform spiroxazine, in which the hydrophobic chain comprised a hexamethylene unit and a 1,4-diazabicyclo[2,2,2]octane unit, and polystyrenesulfonate (PSS) were prepared by self-assembly using layer-by-layer deposition. UV–vis absorbance showed that the bilayer deposition process was linear and highly reproducible. Measurement of the photoinduced ionic conductivity response at 15 °C showed that sufficient reversibility was obtained. High electrolyte concentrations tended to promote surface adsorption.

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