Available online at www.sciencedirect.com
SCIENCE DIRECT®
Dyes and Pigments 72 (2007) 378–382
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Layer-by-layer self-assembled multilayer of cationic spiroxazine and polystyrenesulfonate

Sung-Hoon Kim [a,*], Chang-Ju Shin [a], Sam-Rok Keum [b], Kwangnak Koh [c]

[a] Department of Textile System Engineering, Kyungpook National University, Daegu 702-701, Republic of Korea
[b] Department of New Material Chemistry, Korea University, Jochiwon 339-700, Republic of Korea
[c] Department of Pharmacy, Pusan National University, Pusan 609-735, Republic of Korea

Received 10 February 2005; received in revised form 12 July 2005; accepted 20 September 2005

Abstract

Novel spiroxazine (SO) bearing two positive charges has been synthesized via an improved synthetic route. Alternate multilayer films of an SO and anionic polystyrenesulfonate (PSS) are prepared by self-assembly based on layer-by-layer (LBL) deposition using electrostatic attraction between oppositely charged ions. The build up of the multilayer films is followed by UV–vis spectroscopy and atomic force microscopy (AFM). Photoinduced ionic conductivity response and salt effect of SO/PSS multilayer have been also studied.

Keywords: Spiroxazine; Layer-by-layer deposition; Photochromism; Ionic conductivity; Multilayer

1. Introduction

Ultrathin organic films are of considerable interest because of their potential technological applications in the fields of surface coatings, sensors and optoelectronics [1]. These films are commonly formed using Langmuir–Blodgette (LB) deposition or self-assembly techniques based on chemisorption.

Recently developed electrostatic layer-by-layer deposition has been shown to be a simple and versatile method for assembling thin films [2]. 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 [3–5], dyes [6–9] and biological macromolecules such as DNA [10,11] and proteins [12,13].

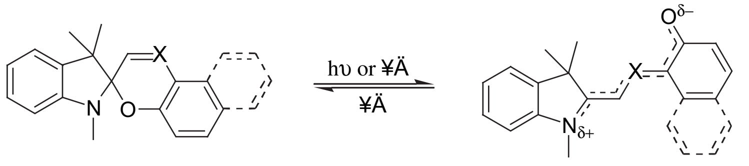
Spiroxazines are photochromic compounds analogous to spiropyrans. These two classes of compounds are similar in many respects. However, the replacement of the benzopyran ring by a naphthoxazine ring results in spiroxazine having the advantage of greatly improved resistance to prolonged UV irradiation, which confers a much more commercial importance to them [14]. On UV irradiation the C–O bond of the colorless spiroxazine is cleaved and the colored merocyanine form is obtained. Thus, the interconversion of spiro (SP)-merocyanine (MC) systems, SP-MC, has been extensively investigated due to their potential applications in molecular devices and uses in biotechnology [15].

We have previously reported the synthesis and self-assembly of the spiroxazine containing alkanethiol with an amide group incorporated into the backbone [16–18]. Also reported has been the photoinduced thickness change of a self-assembled spiroxazine monolayer based on surface plasmon resonance spectroscopy [19]. Here we report the synthesis of a new spiroxazine containing two quaternary ammonium

---

* Corresponding author. Tel.: +82 53 950 5641; fax: +82 53 950 6617.
E-mail address: shokim@knu.ac.kr (S.-H. Kim).

0143-7208/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2005.09.019



(colorless, closed form) (colored, open merocyanine form)

X = CH : spiropyran
X = N : spiroxazine

groups. The cationic spiroxazine synthesized was soluble in a mixture of dimethylsulfoxide (DMSO) and water and used as cationic electrolyte to fabricate thin films by means of an LBL deposition process driven by the electrostatic attractions developed between positively charged SO and negatively charged PSS. The preparation, characterization, and LBL multilayer fabrication of the newly synthesized SO were described.

2. Experimental

2.1. Materials

1,3,3-Trimethyl-2-methyleneindolin, 1-nitroso-2,7-dihydroxynaphthalene, 1,6-dibromohexane, *N*,*N*,*N′*,*N′*-tetramethyl-1, 3-propanediamine (TMPDA), and polystyrenesulfonate (sodium salt, $M_w = 70{,}000$) (PSS) were purchased from Aldrich. The analytical grade solvents were dried with an appropriate drying agent and distilled.

2.2. Synthesis of spiroxazine **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 Refs. [20,21]. 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 suspended powdered potassium carbonate (0.32 g) was refluxed for 24 h. The solution was filtered and then the filtrate was evaporated under reduced pressure. The product obtained was washed with methanol several times and recrystallized from hexane. Yield 63%; mp 147 °C; MS *m*/*z* M^+ 507; ^1H NMR ($CDCl_3$, δ ppm): 1.35 (s, 6H), 1.57 (m, 5H), 1.91 (m, 4H), 3.44(t, $J = 6.52$ Hz, 2H), 4.18 (t, $J = 6.52$ Hz, 2H), 6.57 (d, $J = 7.52$ Hz, 1H), 6.84 (d, $J = 9$ 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 dye **6** (SO)

Dye **4** (4.9 mmol) and 0.32 g (2.46 mmol) *N*,*N*,*N′*,*N′*-tetramethyl-1,3-propanediamine **5** were refluxed in 150 ml 2-methoxyethanol for 48 h. The reaction mixture was cooled to room temperature and 2 l diethyl ether was added. The precipitated dye was suction filtered, washed with ether, methanol and dried. Yield 40%; mp 193 °C; ^1H NMR (DMSO-d_6, δ ppm): 7.84 (s, 2H), 7.82 (s, 2H), 7.76 (d, $J = 9.04$ Hz, 2H), 7.70 (d, $J = 9.04$ Hz, 2H), 7.15 (m, 4H), 7.05 (d, $J = 4.56$ Hz, 2H), 6.91 (d, $J = 9.04$ Hz, 2H), 6.83 (t, $J = 8.04$ Hz, 2H), 6.66 (d, $J = 7.52$ Hz, 2H), 4.14 (t, $J = 6.04$ Hz, 4H), 3.29 (m, 8H), 3.02 (s, 12H), 2.69 (s, 6H), 1.81 (m, 6H), 1.71 (m, 4H), 1.55 (m, 4H), 1.38 (m, 4H), 1.28 (s, 6H), 1.25 (s, 6H).

2.4. Substrate cleaning and multilayer preparation

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 a solution containing 0.16 g SO in a mixture of 14 ml Milli-Q water and 6 ml DMSO for 20 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 a solution containing 0.21 g PSS in 20 ml Milli-Q water. This process is repeated until the desired number of bilayers of SO/PSS is obtained. All adsorption procedures were carried out at room temperature.

2.5. Measurement

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. ^1H 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 by using a Nanoscope IV Multimode. The photographic images were recorded in the conventional height mode (tapping mode, normal AFM). For the measurement of photoinduced ionic conductivity, the device comprised with