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Layer-by-layer self-assembled multilayer film of cationic oligo-(phenylene vinylene) and polyelectrolytes based on electrostatic interaction

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Abstract

Self-assembled multilayer film of a cationic oligo(*p*-phenylene vinylene) derivative, 4,4′-(1,4-phenylene dithenylene)-bis-(*N*-methyl pyridinium iodide) (OPV), and the anionic poly(sodium 4-styrene sulfonate) (PSS) was fabricated by using electrostatic interactions as driving force. X-ray diffraction patterns (XRD) indicate that this method can effectively eliminate the crystallization of OPV. UV–VIS spectra reveal that OPV molecules tend to form H-aggregate in the multilayer film. Fluorescence spectral results show that the luminescent peak of the OPV in multilayer film underwent a blue shift about 80 nm compared with that of OPV in solid state. The emission intensity of OPV in the multilayer film is much stronger than that of OPV in spin-cast film due to the isolation of OPV in the film by PSS.

Keywords: Multilayer; Crystallization; Electrostatic interactions; Luminescent

1. Introduction

Conjugated oligomers have received great attentions in the last few years due to their unique photo-, electro-, and magneto-properties [1,2]. One of the advantages of conjugated oligomers over polymers is their ability to avoid chemical and structural imperfection and to form ordered films. It is well known that the poly(*p*-phenylene vinylene) (PPV) is one kind of the most important electro-photo materials [3–5]. Therefore, the syntheses of high purity oligo(phenylene vinylene) with well-defined structures and related theoretical researches have attracted increasing research interests [1,6,7]. Also, there have been some efforts to study the application potentials of oligo(phenylene vinylene) [8,9]. It has been known that the crystallization of oligo(phenylene vinylene) can affect the properties of devices constructed, such as brightness and stability. Many efforts have been made to solve this problem. In previous studies, oligo(phenylene vinylene) was simply blended with a polymer as dispersion matrix to reduce its crystallization [8,10].

Self-assembly techniques have been extensively explored during the past decades [11,12]. This technique presents some advantages for the construction of multilayer films with controllable film thickness, tunable layer architecture and quantum-size effects [13]. Manipulation of layer-by-layer assemblies from polyelectrolytes and charged dyes has been extensively studied [14,15]. Comparing with the simple blending method, construction of multilayer films with tailored structure via self-assembly may provide a more effective way to optimize the properties of devices based on oligo(phenylene vinylene).

In this report, self-assembled multilayer films of the oligo(phenylene vinylene) derivative 4,4′-(1,4-phenylene dithenylene)-bis-(*N*-methyl pyridinium iodide) (OPV) with poly(sodium 4-styrene sulfonate) (PSS) are fabricated based on electrostatic interactions. The purpose of this work is the elimination of the crystallization of OPV by the self-assembly process, and further the aggregate behavior and luminescent properties of OPV in multilayer films will be discussed.

2. Experimental details

2.1. Synthesis of 4,4′-(1,4-phenylene dithenylene)-bis-(N-methyl pyridinium iodide)

Iodomethane was mixed with γ-methyl pyridine in ethanol under stirring for 0.5 h, a light yellow solution (A) was

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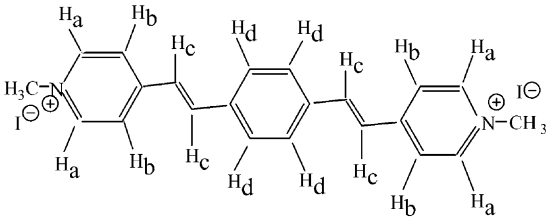

Scheme 1. The molecular structure of OPV.

obtained, then terephthalic aldehyde was added and mixed with a molar ratio 1:2 and refluxed in a NaOH ethanol solution for 60 min. The precipitate was filtered and recrystallized from *iso*-propanol to yield yellow product. ^{1}H NMR (400 MHz, CD_3OD), δ 8.67 ($4H_a$), 7.74 ($4H_b$), 7.13 ($4H_c$), 7.46 ($4H_d$), 2.38 ppm (6H); elemental analysis: calculated for $C_{22}H_{22}N_2I_2$: C 46.48%, H 3.90%, N 4.93%; found: C 45.72%, H 4.01%, N 4.91%. The structure of the synthesized OPV is shown in Scheme 1.

2.2. Fabrication of the multilayer film

Quartz slide was immersed in a H_2O_2/concentrated H_2SO_4 mixture (1:3 in volume) for 30 min, then washed with deionized water for several times to remove all the residues. The treated slide was first modified with aqueous cationic poly(diallyl dimethyl ammanium chloride) (PDDA) to achieve a positively charged surface. Then the substrate was alternately dipped into the water solution of PSS (1 mg/ml) and the water solution of OPV (0.5 mg/ml) (each for 25 min, with an interruption of water rinsing and N_2 drying). The multilayer films can be achieved by repeating the latter two steps in a cyclic fashion.

2.3. Characterization

X-ray diffraction patterns of the sample were obtained on a Rigaku D/max rA diffractometer with the Cu Kα line as radiation ray. UV–VIS absorption spectra were measured by a Shimadzu UV-240 spectrophotometer. Fluorescence spectra were taken on a RF-5301 PC Shimadzu spectrofluorophotometer.

3. Results and discussion

The process of multilayer deposition was monitored by means of UV–VIS spectroscopy. UV–VIS spectra measured during the growing of the PSS/OPV multilayer film are shown in Fig. 1. The absorption maximum at about 360 nm is attributed to π–π^* transition of OPV. The absorption increased along with the increase of the deposition layer number, which indicated that OPV was successfully assembled onto the substrates. The linear increase of the absorption peak with the number of layers shows a continuous deposition process.

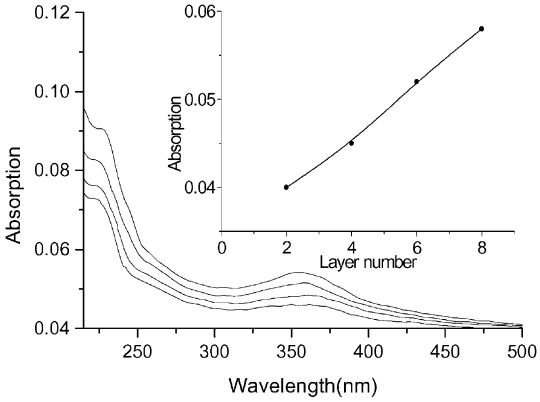

Fig. 1. UV–VIS spectra of multilayer film of OPV/PSS. The number of deposited layer is from 2 to 8, from bottom to top, respectively. Inset: absorbance at 360 nm vs. number of bilayer.

Crystallization of OPV in powder and multilayer film was studied by X-ray diffraction method. The X-ray diffraction patterns (XRD) of OPV powder and the multilayer film are given in Fig. 2(a) and (b), respectively. It can be seen from Fig. 2 that the OPV powder shows a certain crystal character, and the multilayer film is a kind of mesophase. This indicates that the crystallization of OPV has been eliminated when it was combined into the multilayer film.

Generally, the π–π^* transition of molecules in UV–VIS spectra is a useful indicator for studying the aggregation behavior of the molecules. The UV–VIS spectra of OPV multilayer film and OPV in water solution are given in Fig. 3. Compared with the absorption peak at 390 nm in the water solution (the concentration of OPV is very low and there is little aggregation), the π–π^* transition of OPV in the multilayer film appeared at 360 nm. This blue shift indicates that H-aggregates of the OPV were formed in the multilayer film [16]. A possible model for the OPV/PSS alternate self-assembled multilayer film is shown in Fig. 4. The observation of several absorption peaks in the spectrum of OPV spin-casting film indicates that there may exist different aggregates in the casting film. The conclusion that

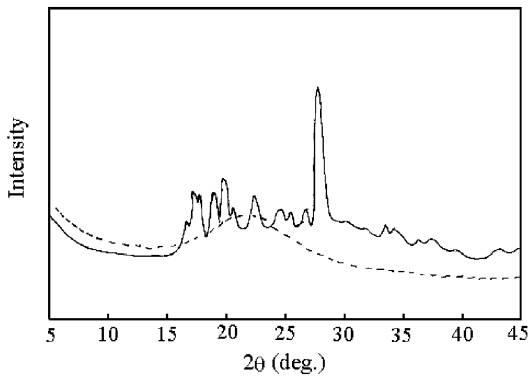

Fig. 2. X-ray diffraction patterns of (a) OPV powder (solid line); (b) multilayer film of OPV/PSS (dashed line).

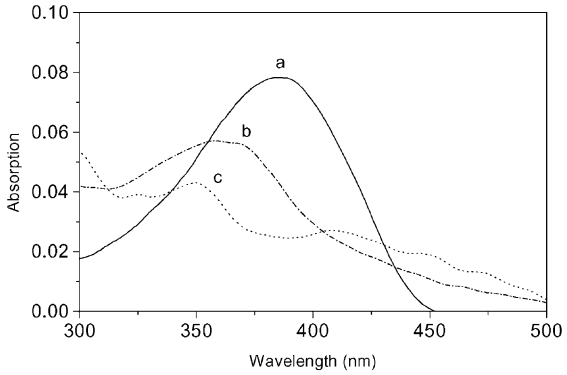

Fig. 3. UV–VIS spectra of (a) water solution of OPV (the concentration is 10^{-5}); (b) multilayer film of OPV/PSS; (c) OPV spin-cast film.

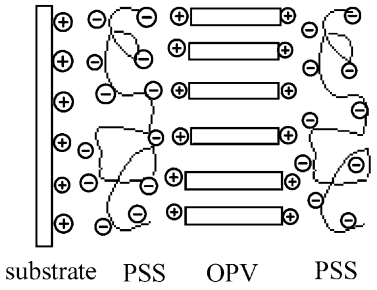

Fig. 4. The proposed model of OPV/PSS alternate self-assembled multilayer film.

self-assembly technique is a promising way to confine OPV in multilayer film, can be drawn.

The fluorescence spectra of OPV in powder, spin-casting film and multilayer film are quite different (see Fig. 5). The spectrum of OPV in water shows a monomeric emission at 475 nm. The luminescent peak of OPV in solid state underwent a red shift compared with that of its water solution, and the peak of the OPV multilayer film underwent a blue shift compared with that of OPV powder. The 1.56° chain torsional angle between adjacent phenylene rings of OPV was calculated by empirical quantum chemistry method AM1, which indicates its coplanar structure. Therefore, it is reasonable to suppose that the coplanar OPV molecules in solid state could be densely packed in a face-to-face manner. This will result in the formation of an excimer, i.e. a complex between an excited state molecule, OPV*, and a ground state molecule, OPV. The excimer formation causes a red shift in emission with respect to monomeric OPV in solution. In the deposition process, the crystallization of OPV was eliminated, the OPV molecules may be interpenetrated by the neighboring polymer layers [17]. This is a reasonable interpretation of its blue-shifted emission compared with that of OPV powder. In the spin-casting film of OPV, the crystallization of OPV was partially eliminated, but OPV alone has a serious self-quenching effect, so it has a very weak luminescence in shorter wavelength region. The dispersion and isolation of OPV in the multilayer film can reduce self-quenching of OPV. Meanwhile, the intersystem crossing effect of I^- ions, which makes the fluorescence quenched [18], can also be eliminated in the deposition process. Therefore, the fluorescence intensity of OPV in the multilayer film is much stronger than that of powder and spin-cast film. The enhanced fluorescence intensity of OPV in the multilayer film is the result of both, the elimination of its crystallization and isolated state in the multilayer film.

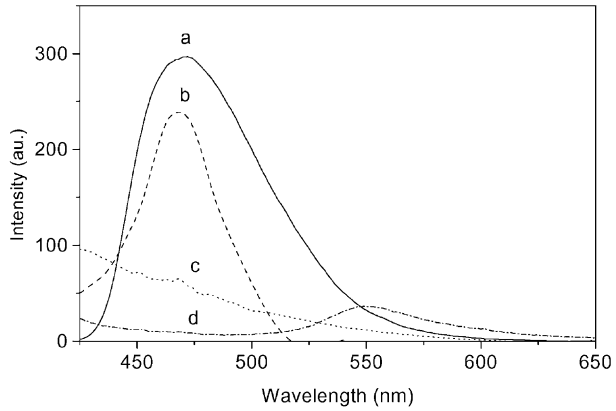

Fig. 5. Fluorescence spectra of (a) multilayer film of OPV/PSS; (b) water solution of OPV; (c) OPV spin-cast film; (d) OPV powder.

In conclusion, the OPV/PSS multilayer film has been prepared by self-assembling method. The deposition process can eliminate the crystallization of OPV. This results in the enhancement of the fluorescence intensity and the blue shift of the fluorescence peak, which makes the multilayer film have practical significance.

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