

# Self-Assembled Film of $Tb^{3+}$ and Poly(3-Thiophene Acetic Acid) via Layer-by-Layer Complexation Technique and Its Photoluminescence<sup>①</sup>

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**Abstract:** The layer-by-layer complexation technique of polymer and metal ion was successfully utilized to fabricate the ultrathin multilayer film of poly(3-thiophene acetic acid (PTAA) and  $Tb^{3+}$  ion by dipping the substrates alternatively in polymer and  $Tb^{3+}$  ion aqueous solutions. UV-vis measurement revealed that the absorbance has linearity with the bilayer number from layer to layer and the X-ray photoelectron spectrum (XPS) confirmed the existence of  $Tb^{3+}$  ion. The pH of both the polymer and  $TbCl_3$  solutions influence the thickness dramatically while the concentration of the solutions is not so sensitive. The luminescent spectrum of the complex film shows the characteristic emission of  $Tb^{3+}$  ion as well as the ligand indicating the formation of the complex.

Key words: rare earths; self-assembly; terbium; complexation; layer-by-layer; photoluminescence

CLC number: O641.4; O482.3 Document code: A Article ID: 1002-0721(2002)05-333-06

Many types of layer-by-layer deposition techniques including electrostatic attraction<sup>[1-3]</sup>, hydrogen bonding<sup>[4,5]</sup>, covalent bonding<sup>[6]</sup>, charge-transfer interaction<sup>[7]</sup> have been exploited for fabricating multilayer films because this type of manipulation has many advantages such as film thickness molecular-level controllable and adaptability of the fabrication process to large-area substrates. A variety of self-assembled films of conjugated polymers<sup>[8-13]</sup> have been constructed for the organic light-emitting devices (OLEDs) since Decher<sup>[14]</sup> and co-workers reported the layer-by-layer deposition technique based on the electrostatic attraction between polycations and polyanions. Self-assembled multilayers through coordination bonding between polymer-based ligands and transition /lanthanide metal ions were first reported by S. K. Tripathy<sup>[15,16]</sup>. This

technique provides the deposition method of insoluble metal-polymer complexes as uniform thin film. This is an interesting approach to improving the properties of OLED by combining the efficiency of metal complexes and the stability and flexibility of polymers<sup>[16]</sup>.

In Tripathy's work, the polymeric ligands are PTAA<sup>[15]</sup> and poly[2-(3-thienyl) ethanol butoxy carbonyl-methyl urethane] (PURET)<sup>[16]</sup>, and the metal ion is  $Eu^{3+}$  ion. the photoluminescence spectra of  $Eu$ /PURET complex film didn't show the characteristic emission of the metal ion except that the luminescence peak at around 610 nm, which is slightly stronger compared to the same spectral region of the spin-coated film. In this contribution, we present the multilayer fabrication of poly(3-thiophene acetic acid) and  $Tb^{3+}$  ion using this layer-by-layer complexation

① Received date: 2002-07-05; revised date: 2002-08-04

Foundation item: Project supported by the State Key Program of Fundamental Research on Rare Earth Functional Materials (G 1998061308, 2001, CCD04300), and NNSFC (20023005)

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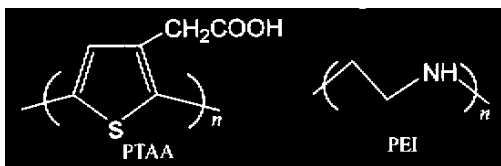
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technique and the factors influencing the film thickness as well as the photoluminescence of the self-assembled film.

## 1 Experimental

### 1.1 Reagents

Poly (3-thiophene-acetic acid) (PTAA) (structure shown in Scheme 1) was prepared by the ferric chloride polymerization of ethyl thiophene-3-acetate (Aldrich) followed by acid hydrolysis of the ester group. Polyethylene amine (PEI) (Scheme 1) (50% water solution, average M. W. 50-6000) obtained from Acros was used without further purification.



Scheme 1: Structures of polymers

PTAA solution was made by dissolving the given amount of polymer by adding sodium hydroxide solution. Its pH was adjusted to a certain value using  $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ HCl}$ . The solution concentration was calculated based on the repeating monomer unit. The PEI solution was made by diluting 50% water solution to 0.1% ( $w/V$ ) by using  $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ HCl}$ . The  $\text{TbCl}_3$  solution was prepared by decomposing the accurate amount of  $\text{Tb}_4\text{O}_7$  (99.99%) with concentrated  $\text{HCl}$  and a small amount of  $\text{H}_2\text{O}_2$  under heating. After  $\text{Tb}_4\text{O}_7$  was completely decomposed, the resulting solution was evaporated to drive out the excessive  $\text{HCl}$  until the pH of the solution reached 4 ~ 5.

### 1.2 Layer-by-layer complexation

Glass slides ( $25 \text{ mm} \times 17 \text{ mm}$ ) were cleaned by placing them in a hot  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$  (7 : 3) bath for 1h firstly and then were ultrasonically agitated in  $\text{H}_2\text{O}/\text{H}_2\text{O}_2/\text{NH}_3$  (5 : 1 : 1) for 30 min. The substrates were extensively rinsed with Millipore water (resistivity was better than  $17.6 \text{ M}\Omega \cdot \text{cm}$ ). After completion of the pretreated steps, the hydrophilic substrates were stored in

water and ready for using.

Multilayer films were fabricated by first dipping the newly hydrophilized glass slides in 0.1% ( $w/V$ ) PEI solution for 20 min at room temperature followed by washing with Millipore water to remove residual polymer and blowing with hot air stream to remove the water membrane adhered on the substrate. Then, the substrates were immersed in the PTAA solution for 5 min, washed and dried as described above. These two steps formed the priming bilayer for the subsequent complex assembly. The substrate covered with the priming bilayer was alternatively immersed in  $\text{TbCl}_3$  and PTAA solutions and was rinsed and dried after each step, such a deposition cycle resulted in one "bilayer" ( $\text{Tb}^{3+}/\text{PTAA}$ ) of complexation. This cycle was repeated  $n$  times to obtain a film of  $n$  bilayers of the self-assembled film, abbreviated as  $(\text{Tb}^{3+}/\text{PTAA})_n$ .

The adsorption kinetics of a single layer of PTAA or  $\text{Tb}^{3+}$  is shown in Fig. 1. The plot in (a) is the time - absorbance curve of  $\text{Tb}^{3+}$

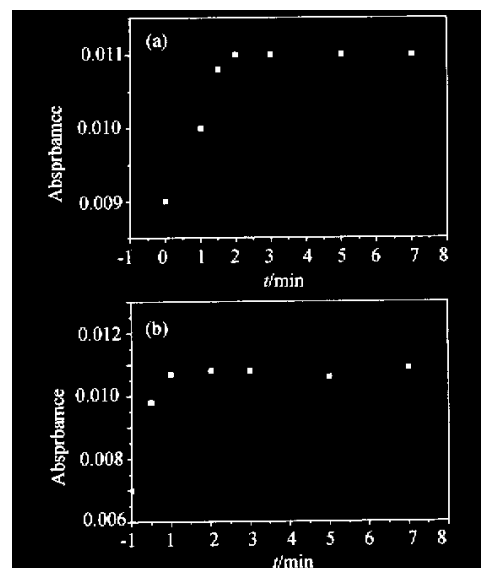


Fig. 1 Time-dependent adsorption behavior (visible absorption measured at 400 nm)

(a) A single adsorbed layer of  $\text{Tb}^{3+}$  deposited on the priming bilayer by fixing the dipping time of PTAA 10 min; (b) A single PTAA layer deposited on the first metal layer by fixing the dipping time of  $\text{TbCl}_3$  solution 10 min

ion deposited on the priming bilayer by fixing the dipping time of PTAA 10 min. Fig. 1(b) shows the time-absorbance curve of PTAA coordinated to the first  $Tb^{3+}$  ion layer whose dipping time was fixed at 10 min. The plots indicate that the absorbance of each layer reached a plateau within 2 min. The dipping time of all the experiments presented in this paper is 2 min for each layer at room temperature.

### 1.3 Characterization

UV-visible absorption spectra were recorded using a SHIMADZU 3100 UV-VIS-NIR spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurement was performed using a VG ESCALAB 5 multi-technique electron spectrometer, using Al K $\alpha$ X-ray as a radiation source, and the luminescence spectra were measured using a F-4500 HITACHI fluorescence spectrophotometer.

## 2 Results and Discussion

### 2.1 Fabrication of complex film

The fabrication process of the self-assembled film was monitored by visible absorption spectrometer. Results shown in Fig. 2 indicates that the deposition process is completely reproducible from layer to layer. The linearity of the plot of absorbance against the number of bilayers (measured at 400 nm here and else where) demonstrates that each bilayer contributes an equal amount of PTAA to the film. The complex film can be successfully assembled to more than 50 bilayers.

XPS is a powerful means to detect metal ion in the film. Fig. 3 shows the XPS spectrum taken from a film of 7 bilayers  $(Tb^{3+}/PTAA)_7$ . The binding energy of Tb4d peaks at 155 eV, shifted 5 eV compared with the neutral atom (150 eV)<sup>[17]</sup>, and this shift may be caused by the different chemical environments between  $Tb^{3+}$  ion and the neutral Tb atom. This result confirmed the existence of  $Tb^{3+}$  ion.

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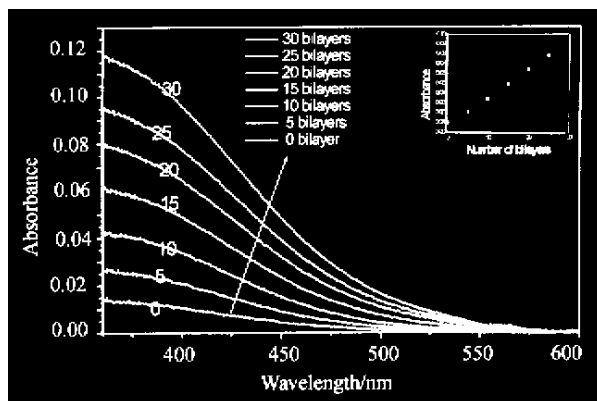


Fig. 2 Absorption spectra of multilayer thin films with an increasing number of bilayers (0 indicates the absorption of the priming bilayer) PTAA solution:  $5 \text{ mmol} \cdot \text{L}^{-1}$ , pH 4.5;  $TbCl_3$  solution:  $5 \text{ mmol} \cdot \text{L}^{-1}$ , pH 4.5. Inset is the absorption intensity (measured at 400 nm) vs. the number of bilayers

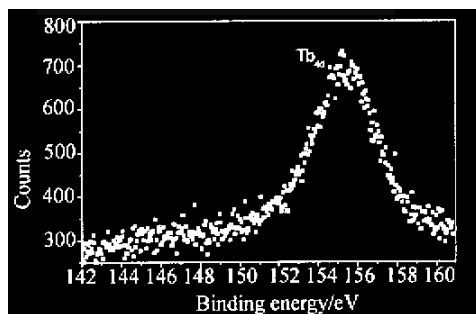


Fig. 3 XPS spectrum for the Tb4d electrons from a film of  $(Tb^{3+}/PTAA)_7$  fabricated from  $5 \text{ mmol} \cdot \text{L}^{-1}$  (pH 4.5) PTAA solution and  $5 \text{ mmol} \cdot \text{L}^{-1}$  (pH 4.5)  $TbCl_3$  solution

### 2.2 Concentration effect

Fig. 4 (a) shows the plot of absorbance intensity against the number of bilayers at different concentration of PTAA solution while  $TbCl_3$  solution was fixed at  $5 \text{ mmol} \cdot \text{L}^{-1}$  and pH 4.5. Fig. 4(b) is the effect of  $TbCl_3$  solution concentration, where the ligand solution was fixed at  $2 \text{ mmol} \cdot \text{L}^{-1}$  and pH 4.5. The film thickness is slightly increased as the ligand concentration increased, and this is accordant to what the literature reported<sup>[18]</sup>, as in higher concentration the polymer tends to aggregate which leads to the increment of the polymer adsorbed on the substrate. But the concentration of  $TbCl_3$  solution has no sensitive effect on the film thickness in the selected period.

### 2.3 pH effect

The film thickness was found to be strongly dependent on the pH values of both PTAA and  $TbCl_3$  solutions as shown in Fig. 5. The amount of PTAA adsorbed on the substrate for a given PTAA concentration ( $2 \text{ mmol} \cdot \text{L}^{-1}$ ) increased as its pH value decreased (Fig. 5 (a)) and reached the maximum when its pH = 4.5, where for the  $Tb^{3+}$  ion solution the concentration is  $5 \text{ mmol} \cdot \text{L}^{-1}$  and pH value is 4.5. This result is not contradictory to the fact that the amount of weak polyelectrolyte adsorbed onto a charged surface reaches the maximum at pH value about one unit below the  $pK_0$  ( $K_0$  is the ionization equilibrium constant) of the polymeric acid<sup>[19]</sup>, if it is assumed that the  $pK_0$  value of PTAA is similar to that of related polyacid ( $pK_0 = 4.3 \sim 4.9$ )<sup>[18]</sup>. However, the solution tends to precipitate when pH value is lower than 4.5, so this is the lowest limit of our experiments. This pH dependence is related to the change in the ionization degree of the carboxylic acid groups. When pH increases, the net negative charges of the polymer increase, so the polymer chain would be much straight caused by the electronic repulsion of the negative charge between the carboxylic acid anions, which leads to thinner layer. Under lower pH value, the polymer would be coil that leads to the thicker layer. When PTAA solution was fixed at  $2 \text{ mmol} \cdot \text{L}^{-1}$  pH 4.5 and the concentration of the  $TbCl_3$  solution was  $5 \text{ mmol} \cdot \text{L}^{-1}$ , the deposited amount of PTAA per layer tends to increase as the number of bilayers increased when the pH of the  $TbCl_3$  solution above 5.5 (the upper two plots in Fig. 5 (b)). The reason is not clear now, a reasonable explanation may be as follows: under higher pH conditions, the partial hydrolysis of terbium ion may take place, more terbium ions will exist as  $[Tb(OH)(H_2O)_n]^{2+}$  and  $[Tb(OH)_2(H_2O)_n]^+$  but rare of them exist as  $[Tb(OH)_3(H_2O)_n]^{3+}$ . From the viewpoint of charge equilibrium, for a certain negative charged surface, it would absorb more  $[Tb(OH)(H_2O)_n]^{2+}$ ,  $[Tb$

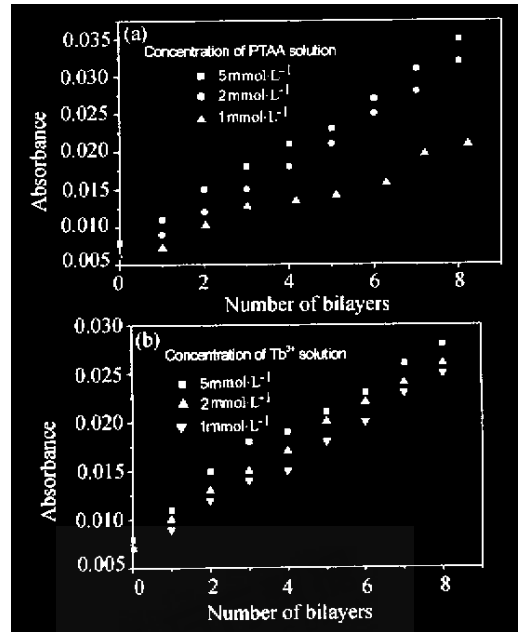


Fig. 4 Influence of concentration on the visible absorption (measured at 400 nm) versus number of bilayers (a) ligand solution effect (PTAA: pH 4.5;  $TbCl_3$  solution: pH 4.5,  $5 \text{ mmol} \cdot \text{L}^{-1}$ ); (b)  $TbCl_3$  solution effect ( $TbCl_3$  solution: pH 4.5; PTAA: pH 4.5,  $2 \text{ mmol} \cdot \text{L}^{-1}$ )

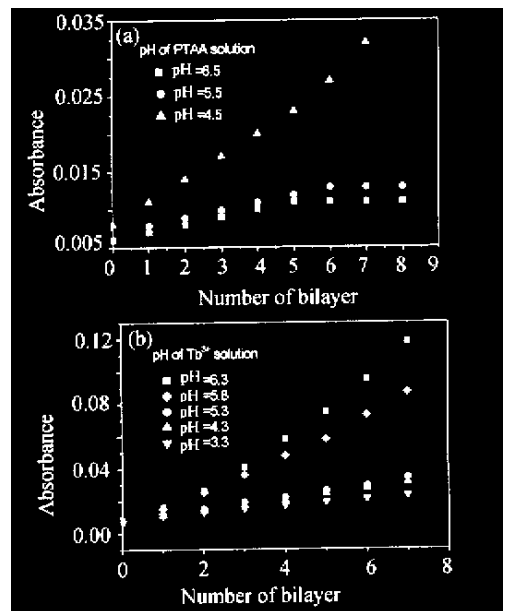


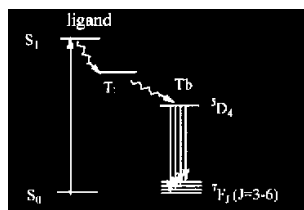
Fig. 5 Influence of pH on the visible absorption (measured at 400 nm) versus number of bilayers (a)  $2 \text{ mmol} \cdot \text{L}^{-1}$  PTAA solution ( $TbCl_3$  solution was fixed at pH 4.5,  $5 \text{ mmol} \cdot \text{L}^{-1}$ ); (b)  $5 \text{ mmol} \cdot \text{L}^{-1}$   $TbCl_3$  solution (PTAA solution was fixed at pH 4.5,  $2 \text{ mmol} \cdot \text{L}^{-1}$ )

$(OH)_2(H_2O)_n]^+$  species existing under higher pH than  $[Tb(H_2O)_n]^{3+}$  existing under lower pH. After surface neutralization reaction, more terbium ions are ready for absorption of PTAA in the former condition than in the later condition and consequently lead the amount of PTAA deposited onto the surface increases.

## 2.4 Photoluminescence

The films for the photoluminescence (PL) measurement were fabricated on quartz slides. The PL of the ligand solution and the self-assembled polymer film of (PTAA/PEI) were measured to compare with the complex film. The film  $(Tb^{3+}/PTAA)_{18}$  was made from  $Tb^{3+}$  ion solution ( $5 \text{ mmol} \cdot \text{L}^{-1}$  and  $\text{pH} = 6.0$ ) and the ligand solution ( $5 \text{ mmol} \cdot \text{L}^{-1}$  and  $\text{pH} = 5.3$ ) while the (PTAA/PEI) 20 film was fabricated by electrostatic deposition from 0.1% ( $w/V$ ) PEI solution and the same PTAA solution as used in fabricating the complex film. Fig. 6 shows the UV-vis absorbance spectra (a) and PL spectra (b) of the ligand solution, (PEI/PTAA) 20 film and  $(Tb^{3+}/PTAA)_{18}$  film. Both films have the same UV-vis character as the ligand solution. PL spectra of the two films show red shift compared to the ligand solution, this shift is caused by the conformational changes that polymer main chains undergo in the deposition and dipping process<sup>[15]</sup>. The complex film  $(Tb^{3+}/PTAA)_{18}$  exhibits the characteristic emission peaks of  $Tb^{3+}$  ion except the ligand luminescence, the four peaks at 489, 545, 584, 612 nm are assigned to  $^5D_4 \rightarrow ^7F_6$ ,  $^5D_4 \rightarrow ^7F_5$ ,  $^5D_4 \rightarrow ^7F_4$ ,  $^5D_4 \rightarrow ^7F_3$  transition of the 4f electron in trivalent  $Tb^{3+}$  ion<sup>[20]</sup> respectively. The appearance of the characteristic luminescence of  $Tb^{3+}$  ion is because the exciting triplet energy of the ligand matches the  $^5D_4$  energy level of  $Tb^{3+}$  ion. The 4f electrons can be excited to  $^5D_4$  orbital<sup>[21]</sup> (Scheme 2), when they decay to related ground states  $^7F_3$ ,  $^7F_4$ ,  $^7F_5$  and  $^7F_6$ , they emit fluorescence. Although the PL is relatively weak compared with other rare earth complexes<sup>[22]</sup>, it

was several times stronger than (PEI/PTAA) film, and also it became narrow, which is important in OLEDs, this makes the film have the potential application in OLEDs.



Scheme 2

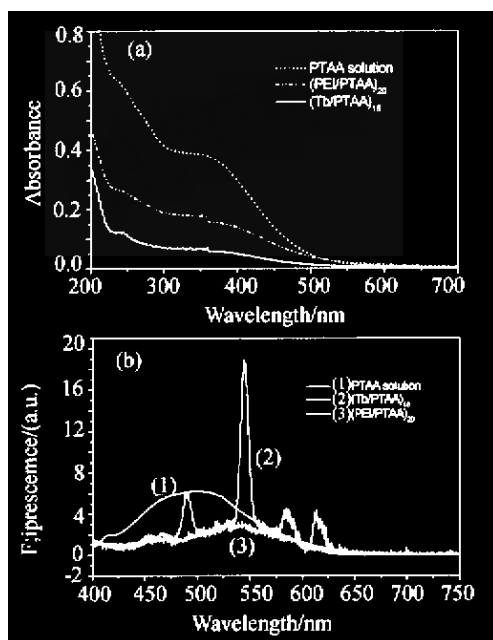


Fig. 6 Normalized UV-vis (a) and PL spectra (b) of ligand solution, (PEI/PTAA)<sub>20</sub> film and  $(Tb^{3+}/PTAA)_{18}$  film

Solution:  $\lambda_{ex} = 330 \text{ nm}$ ; (PEI/PTAA)<sub>20</sub> film:  $\lambda_{ex} = 330 \text{ nm}$ ;  $(Tb^{3+}/PTAA)_{18}$  film:  $\lambda_{ex} = 300 \text{ nm}$

## 3 Conclusions

The multilayer thin films employing poly(3-thiophene acetic acid) and  $Tb^{3+}$  ion have been successfully fabricated. The successful fabrication has been confirmed by UV-vis spectra, XPS and PL. The process parameters such as pH and concentration of both ligand and metal ion solutions affected the thickness of films to a different extent, which could be explained by the conformational change and the weak electrolyte nature of the polymer. The PL spectrum of the film shows the characteristic emission of  $Tb^{3+}$  ion as

well as the ligand emission. This is the first time we observed the metal ion luminescence from the self-assembled film of polymeric ligand and the rare earth ion, which makes it have the potential application in OLEDs.

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