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Novel Layer-by-layer Complexation Technique and Properties of the Fabricated Films

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A novel layer-by-layer complex-fabrication technique for multilayer film assembly was developed by alternatively dipping desired substrates in macromolecular ligands and Eu^{3+} ion solutions. A water-soluble, luminescent thiophene-based polymer, viz., poly[2,5-(3-carboxymethyl urethanyl ethyl) thiophene] (*H*-PURET), was prepared and used as the macromolecular ligand. Multilayer deposition was monitored using UV-visible spectroscopy by following the absorbance increase due to the deposition of the polymer layer. Multilayer thin films were characterized using infrared and fluorescence spectroscopic techniques, transmission electron microscopy (TEM), and energy-dispersive X-ray spectrometry (EDXS). The conductivity and the electroluminescence properties of the conjugated polymer−Eu^{3+} complex multilayer films were also measured. The observed electroluminescence intensity of conjugated polymer−metal complex multilayer film was about 2 times higher than for the conjugated polymer by itself. The approach is general in that other macroligands and metal ions may be employed.

1. Introduction

During the past several years, layer-by-layer deposition techniques have attracted a great deal of attention as effective methods to prepare uniform, ultrathin structures. Since composition, thickness, and orientation of each layer can be manipulated using this technique, it provides a route for the formation of various ordered structures at the molecular level.[1−5] This manipulation at the molecular level offers many potential advantages in device applications, including use as active components in nonlinear optical devices,[2,6] employing materials with selective chemical responses for sensor applications,[5] stable charge-separated assemblies for photovoltaics,[7] and light-emitting diodes.[8]

Since the first report of Decher and co-workers,[9] there have been numerous reports on the layer-by-layer deposition techniques based on the electrostatic attraction between polycations and polyanions. Other types of intermolecular interactions, including hydrogen bonding,[10,11] covalent bonding,[6,12−16] and charge-transfer interactions,[17] have also been exploited for fabricating multilayer films. Coordination bonding is another type of intermolecular interaction that has been used to fabricate self-assembled monolayer and multilayer films of monomeric, multidentate ligands with transition metal ions.[18−24] Monolayer films of thiols-copper (II) and

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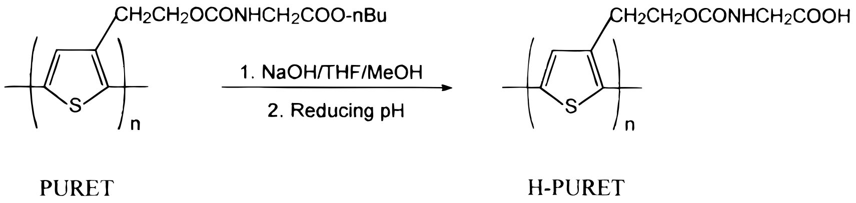
Scheme 1. Preparation of *H*-PURET



alkylamine acetate-Ru (II) have been fabricated by combining thermally induced deposition techniques with self-assembly chemistry via coordination bonding.[18,19] Multilayer films employing coordination reactions, such as bipyridine ligands with Ni(II);[20] resorcinol ligands with Fe(II), Co(II), Cu(II), Zn(II), and Cd(II);[21] diisocyanide ligands with Co(II);[22,23] and bis(hydroxyquinoline) ligands with Zn(II)[24] have been reported. Complexation reaction is a powerful technique for fabricating thin films with well-controlled thickness from insoluble metal−organic complexes. The aforementioned studies are, however, based on monomeric ligands and, to the best of our knowledge, there is no report on employing macromolecular ligands for layer-by-layer deposition.

This report describes an approach to fabricating self-assembled multilayers through coordination bonding between polymer-based ligands and transition/lanthanide metal ions. This technique provides several advantages, such as ease of processing, the ability to control thickness at the molecular level, adaptability of the fabrication process to large area substrates, and deposition of insoluble metal−polymer complexes as uniform thin films. Such thin films have potential applications as electronic and optical components, including thin-film conducting channels in devices and organic light-emitting diodes.

In this manuscript, we describe the fabrication of multilayer thin films from conjugated polymers and lanthanide (europium) ions by employing the layer-by-layer complex-fabrication technique. A water-soluble, fluorescent, conjugated polymer, poly[2,5-(3-carboxymethyl urethanyl ethyl) thiophene] (*H*-PURET), was prepared. *H*-PURET polymer was employed as the macromolecular ligand to complex with Eu^{3+} ions during multilayer thin film deposition. We report on the fabrication of the multilayers and the properties, such as conductivity, photo-, and electroluminescence (EL) characteristics of fabricated multilayer thin films employing the layer-by-layer complexation technique.

2. Experimental Section

2.1. Materials. Poly[2-(3-thienyl)ethanol butoxy carbonyl−methyl urethane](PURET) was prepared as reported.[25] Europium (III) chloride hexahydrate and other chemicals used in this study were purchased from Aldrich Chemical Co., Inc., and were used without further purification. Conducting polyaniline (emeraldine salt form) was obtained from Allied Signal and was used without further treatment.

2.2. Preparation of Poly[2,5-(3-carboxymethyl urethanyl ethyl) thiophene] (*H*-PURET). PURET polymer was dissolved in tetrahydrofuran (THF) (1.0 g in 100 mL) and was taken in a round-bottomed flask fitted with a reflux condenser and a magnetic stirring unit. The temperature of the bath was raised to 40 °C. Saturated NaOH solution in methanol (about 10 drops) was added slowly to the PURET solution, while stirring vigorously. A bright red precipitate appears upon adding the sodium hydroxide solution. The precipitate was filtered and repeatedly washed with THF. The precipitate is the sodium salt of hydrolyzed PURET (*H*-PURET) and is soluble in water. *H*-PURET was precipitated from water (by reducing the pH of the solution) and filtered. The precipitated *H*-PURET was washed with water and dried under vacuum. *H*-PURET is soluble in *N*,*N*-dimethylformamide (DMF), 1-methyl-2- pyrrolidinone (NMP), and water at high pH. However, once the polymer is dissolved in water, the pH can be reduced to about 4.0 without precipitation. Fourier transform infrared (FT-IR) (KBr, cm^{-1}): 3515 (s, ν_{O-H}, carboxylic acid), 3325 (s, ν_{N-H}), 3116 (s, ν_{C-H}, thiophene ring), 2967 and 2865 (s, ν_{C-H}, aliphatic), 1720 (s, $\nu_{C=O}$, carboxylic acid), and 1705 and 1690 (s, $\nu_{C=O}$, urethane carbonyl), 1526 (w, $\nu_{C=C}$), 837 (ν_{C-H} out of plane, thiophene ring). ^1H NMR (DMSO-*d*6, δ in ppm): 12.43 (broad, s, 1H, $-COOH$), 7.34 and 7.28 (1H, thiophene ring), 4.32 and 4.19 (2H, $-CH_2-$, respective head-to-tail coupling, and head-to-head and tail-to-tail coupling defects), 3.75 (broad, s, 1H, $-NH-$), 3.67 (s, 2H, $-CH_2-$), 3.12 (1.3 H, $-CH_2-$, head-to-tail coupling), 2.83 (0.7 H, $-CH_2-$, head-to-head and tail-to-tail coupling defects).

The number- and weight-average molecular weights were calculated as 42,800 and 276,000 g/mol, respectively. The hydrolysis of PURET is shown in Scheme 1.

2.3. Layer-by-Layer Complexation. *2.3.1 Surface Cleaning and Hydrophilization.* Slide glass (25 mm × 75 mm) was hydrophilized using 1% Chem-solv solution (aqueous alkaline alcohol) treatment and used as substrate.[26] The slides were washed in 1% Chem-solv solution in deionized (DI) water with ultrasonication to generate anionic charges on the surface by partial hydrolysis. After 180 min of this treatment, slides were rinsed with water in an ultrasonicator for 30 min. Rinsing was repeated twice. DI water from a Milli-Q system (resistivity of 18.2 MΩ* cm, organic contents less than 10 ppb) was used in all the experiments. The cleaned, hydrophilized glass slides were used as substrates for monitoring multilayer deposition.

A transparent indium−tin-oxide (ITO) coated glass slide was converted to a hydrophilic surface as described above, and a molecular layer of polycation was adsorbed onto the ITO substrate by electrostatic interactions.[27]

2.3.2. Layer-by-Layer Complex-Fabrication of Polymer−Metal Multilayers. The concentrations of the polymer solutions were calculated based on their repeating units. Hydrophilized glass slides were immersed in 1 mM poly (diallyldimethylammonium chloride) (PDAC) solution (pH 6.5) for 10 min at room temperature and then washed with buffered DI water (pH 6.5). After the slides were removed from the wash solution, a stream of nitrogen was blown over the film surface until the adhering water layer was completely removed. The slide was dipped into an aqueous solution of the bidentate ligand (carboxylic acid

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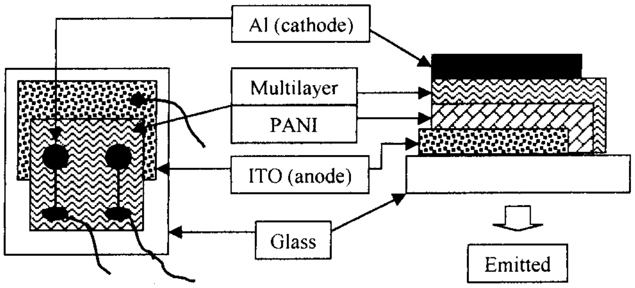

Figure 1. Polymer light-emitting diode (LED) configuration.

in *H*-PURET, 1mM, pH 6.5) functionalized thiophene polymer, and a molecular layer of the polymer was adsorbed onto the slide by electrostatic interaction. This type of multilayer assembly using electrostatic interactions has been well studied.[27] This bilayer from the polycation and polyanion is a priming layer needed for the subsequent layer-by-layer complexation process. The exposed bidentate ligands in the slide were treated with Eu^{3+} metal ion solution followed by alternating treatment of the slide with polymer solution and metal ion solution to form stable complex multilayers.

2.4. Characterization. IR spectra were recorded on a Perkin–Elmer 1760X FT-IR spectrometer using KBr pellet. UV–visible spectra were recorded using a GBC UV/VIS 916 spectrophotometer. Emission characteristics of the samples were measured using a SLM-AMINCO Model 8100 spectrofluorometer from 500 to 700 nm. A sample for transmission electron microscopy (TEM, Philips EM 400T) was made on collodion film according to literature.[28] Energy-dispersive X-ray spectrometry (EDXS, Tracor Northern TN5500) was used to obtain information on the elemental composition from the multilayer films. Thickness of the thin films was measured using atomic force microscopy (AFM, Park Scientific, SFM-BD2, and STM-SA1) and ellipsometry (Rudolph Research, Auto EL ellipsometer). The molecular weights of polymers were determined employing gel permeation chromatography (GPC, Waters Model 510 pump, and Waters 410 refractive index detector) with styragel columns relative to polystyrene standards using dimethylformamide (DMF) as an eluent. The column was injected with 100 μL of the polymer solution in DMF (1 mg/mL) and was eluted with DMF.

2.5. Conductivity Measurement. Multilayer and spin-coated films were prepared on the clean, pre-patterned ITO substrates. To reexpose a part of the ITO substrate for electrode attachment, a small spot on the film was cleared by a swab of glass wool soaked with sulfuric acid and subsequently washed with DI water followed by dry nitrogen blowing. The film was dried in a vacuum at room temperature for 48 h prior to use. Copper wire electrodes were attached to the ITO surface using silver pastes. Conductivity of each film was calculated from its resistance value measured by a Keithley 619 Electrometer/Multimeter.

2.6. Electroluminescent (EL) Device Fabrication. Polyaniline (PANI) was incorporated as a hole-transporting layer into the device.[29,30] PANI was dissolved in trifluoroacetic acid (TFA, 2 wt %/vol), filtered through 0.2 μm Gelman filters, and spin-coated on ITO glass slides (1000 Å thickness; surface resistivity of 10 $\Omega \times cm^2$). *H*-PURET (5 mM solution in water) was deposited onto this PANI-coated ITO slide by spin coating (535 Å thickness). In the case of multilayer films, PANI-deposited ITO slides were used as substrate to build multilayers. The ITO-coated glass slides were patterned before coating PANI and *H*-PURET or multilayer films, as shown in Figure 1. Finally, a 500 Å thick Al film was deposited on top of the spun-cast PURET or the multilayer films by thermal evaporation to form the LED device as shown in Figure 1.

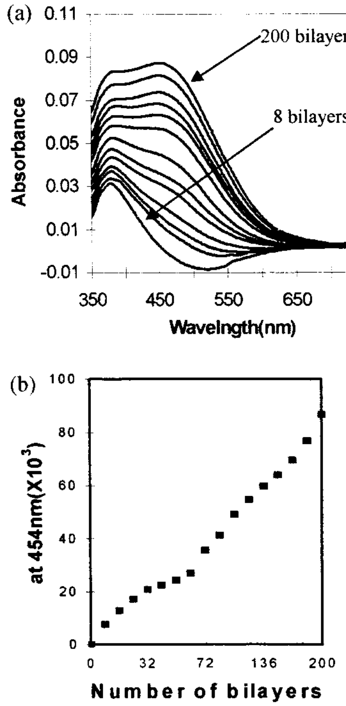

Figure 2. (a) Absorption of multilayer films deposited on ITO (from 8 to 200 bilayers). (b)Net absorbance (absorbance of multilayer–absorbance of priming layer) vs number of bilayers.

3. Results and Discussion

3.1. Characterization of Multilayer Films. Layer-by-layer conjugated polymer–metal ion complexation process was used to build thick multilayers by alternatively dipping the desired substrates in metal ion and polymer macroligand solutions. Multilayer films were fabricated using the *H*-PURET solution in water (5 mM; at pH 6.5) and aqueous europium chloride solution (5 mM; at pH 5.5) at 50 °C. The experimental conditions were optimized, expanding upon our previously reported results.[31] The absorbance at 454 nm due to the polymer increased linearly with the number of bilayers deposited. We have successfully fabricated up to 200-bilayer-thick multilayer films employing the layer-by-layer complexation–fabrication technique, while maintaining the linearity in absorbance (Figure 2). Much thicker films can be obtained by optimizing process conditions such as pH and temperatures of the solutions.

Infrared spectroscopy (IR) was used to characterize the complexation between *H*-PURET and Eu^{3+} ions. The strong absorption bands at 1580 and 1450 cm^{-1} in the IR spectrum of multilayer film correspond to asymmetric and symmetric stretching of coordinated carboxylate ($-COO^-$) groups. The presence of these bands, which are absent in the *H*-PURET polymer, indicates the coordination bonding between carboxylate groups of the polymer and Eu^{3+} ions (Figure 3).[32]

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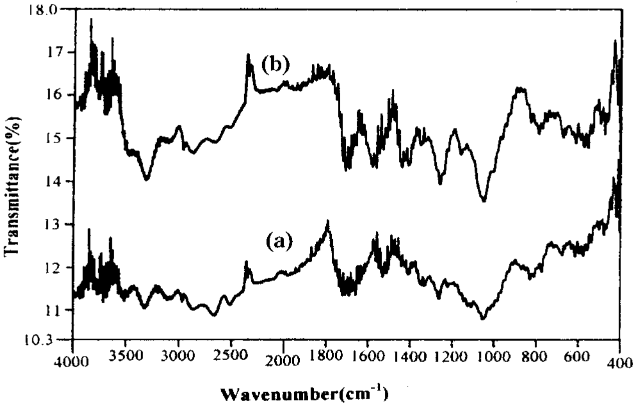

Figure 3. Infrared spectra of (a) *H*-PURET and (b) multilayer films of *H*-PURET and Eu(III).

Transmission electron microscopy (TEM) and energy-dispersive X-ray spectrometric (EDXS) techniques were used to obtain further complementary evidence of the growth of multilayer films (Figure 4). Multilayer films for TEM were deposited on collodion films. Due to the irregularity of the collodion base films, which were cast from amyl acetate solution, the thickness of the multilayer films deposited on top visually appeared to be irregular. From the EDXS results, however, uniform growth of the multilayer film over large areas was clearly established. The complex formation can be identified by comparing peaks due to europium from the complex and sulfur from the polymer. The amounts of europium and sulfur atoms are higher in the thicker spots (B in (a) and (c) of Figure 4) compared to the uniform region (A in (a) and (b) of Figure 4), while the ratio of europium to sulfur is similar in both thick and thinner regions. This result shows that the multilayer complexes were deposited with uniform stoichiometry throughout the substrate.

UV−visible spectra of the polymer solution (in DMF), spin-coated polymer film, and multilayer polymer−Eu^{3+} complex film (20 bilayers) were compared (Figure 5). The absorption maximums for polymer solution, spin-coated film, and multilayer film are ca. 403, 437, and 444 nm, respectively. The shift in absorption maximum in going from solution to solid film is caused to a certain extent by the conformational changes that polymer main chains undergo in the deposition and dipping process. Although polythiophene is a conjugated polymer, conformation change in the main chain may occur due to a variety of factors, including conjugation defects and the presence of large flexible side groups.[33] *H*-PURET has urethane segments in the side chain, which can form intramolecular hydrogen bonding. This side chain hydrogen bonding helps to extend the effective conjugation length of the main chain by restricting the twisting of the main chain in the solid state.[34] In solution, especially in polar solvents, e.g., DMF, the hydrogen bonding is broken due to solvation of the side groups by the polar solvent molecules. As a result, the effective conjugation length is reduced, resulting in blue shift of the absorption maximum in the solution ($\pi \rightarrow \pi^*$ transition).

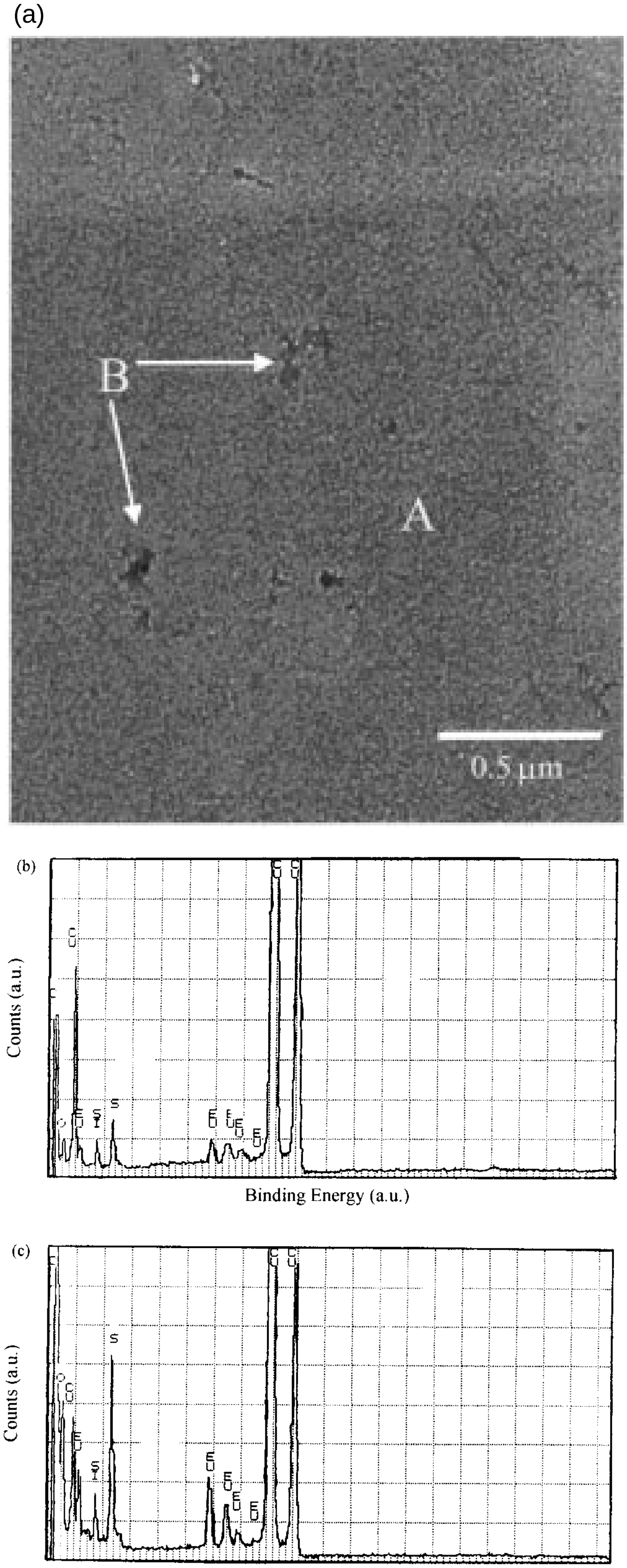

Figure 4. TEM picture and EDXS spectra of multilayer film. (a) TEM picture, A: uniform region, B: thicker region; (b) EDXS spectrum of region A; (c) EDXS spectrum of region B.

3.2. Conductivity. Conductivity was calculated according to following equation:

$$\text{Conductivity} = \frac{1}{\rho} = \frac{l}{R \times A} \qquad (1)$$

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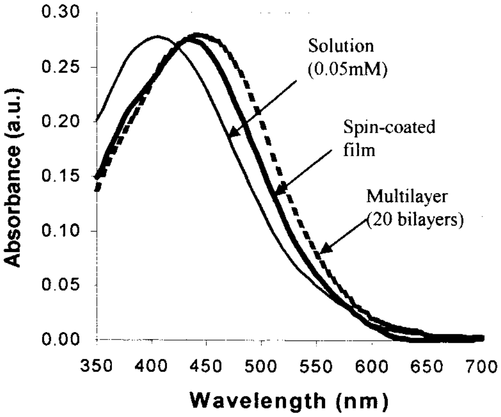

Figure 5. UV-visible spectra of polymer solution, polymer spin-coated film, and multilayer (20 bilayers).

where ρ is the resistivity of the conductor; l is the length of the conductor; A is the cross-sectional area; and R is the resistance measured by electrometer.

It was difficult to accurately establish the thickness of the multilayer film by ellipsometry, due to two distinctly different refractive indices of the component materials (polymer and europium) in the thin film. Therefore, we used atomic force microscopy (AFM) and UV-visible absorbance measurements to estimate the thickness of the film. Since the molar absorptivity of the film from the same material is constant at a given wavelength and the concentration of the chromophores in the multilayer is almost independent of the number of layers under the same deposition conditions, the absorbance of a film is proportional to its thickness. Therefore, the film thickness can be estimated from a known thickness using the equation

$$A = \epsilon \cdot c \cdot l = \alpha \cdot l \qquad (2)$$

where ϵ is molar absorptivity; c is the concentration of chromophore in the film; l is the path length (thickness of the film); and α is a constant (product of molar absorptivity and concentration of chromophore).

We measured the thickness and the absorbance of a multilayer film using AFM and UV/visible spectrophotometry and estimated the thickness of other thin films by extrapolation.

Three different types of films were prepared: multilayer films of *H*-PURET and Eu^{3+}, multilayer films of *H*-PURET and PDAC (electrostatic layer-by-layer complexation), and *H*-PURET spin-coated films from DMF solution (Table 1). The conductivity of the multilayer films of *H*-PURET and Eu^{3+} are about an order of magnitude higher than the other two types of films. Better order and improved transport properties of the metal ion–ligand complex in the multilayers is anticipated. The higher conductivity of the multilayer films may, however, also include contribution from the presence of ions from the residual sodium carboxylates of the polymer. These ions are absent in spin-coated film.

3.3. Electroluminescence of multilayer films. Electroluminescent (EL) devices from organic materials have attracted considerable interest since Tang and VanSlyke[35,36] introduced injection-type EL devices based on sublimed organic materials, because of their potential applications in display technologies.[37–40]

Luminescent complexes based on lanthanide metal ions (terbium and europium, among others) have attracted considerable interest and have been incorporated into EL devices. These ions possess long excited-state lifetimes, narrow emission (<10 nm full width at half-maximum), large Stokes shifts (>150 nm), and high quantum yields (~1).[41–43]

Conjugated polymers such as poly (phenylene vinylene) have provided an interesting approach to realizing the potential for EL device applications.[44–47] Employing polymeric materials rather than low-molecular-weight materials would minimize the “crystallization effects” and the resultant degradation of the electroluminescent devices.

Layer-by-layer complexation between macromolecular ligands and lanthanide metal ions is an interesting approach to improving the properties of organic light-emitting diodes (OLEDs) by combining the efficiency of metal complexes and the stability and flexibility of polymers. This technique offers a simple and economic process especially for large-area substrates, regardless of their shapes. In addition, a large variety of metal complexes, including insoluble metal complexes, can be incorporated homogeneously as a thin film into flexible substrates. We have investigated the EL of the multilayer films to further examine the properties and potential applications of this approach.

EL of spin-coated polymer films and layer-by-layer complex deposited multilayer films was measured. The measurements were carried out in a black painted box to prevent background light contributing to the EL signal and under a nitrogen environment to avoid possible oxidation of the polymer. Polyaniline was used as a hole transport layer in the fabrication of EL[29,30] devices.

The EL signal of a spin-coated film of pure polymer (*H*-PURET) was measured to compare with that of the multilayer film and to investigate the effect of the complex (Figure 6). Prior to the EL measurement, fluorescence behavior of the polymer solution, the spin-coated film, and the multilayer film was measured and compared to understand the contribution of the complex to the electroluminescence of the multilayer film (Figure 7). The intensity scale of the curves in Figure 7 is arbitrary, because the data was scaled to compare the curve shapes and emission maxima.

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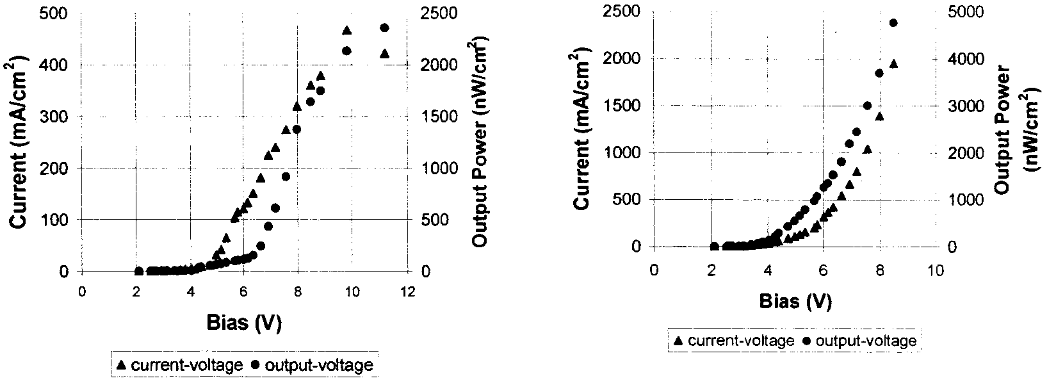
Table 1. Conductivity of Spin-Coated Film and Multilayer Films

	film		absorbance[d]	thickness, Å	width of etched line, cm	width of substrate, cm	cross-sectional area, cm^2	resistance, Ω	conductivity[h], S/cm
1	multilayer film[a]	10 bilayers	0.0706	173[f]	0.14	2.55	4.412×10^{-6}	1.886×10^{8}	1.682×10^{-4}
2		20 bilayers	0.1235	328[e]	0.15	1.55	5.084×10^{-6}	1.724×10^{8}	1.711×10^{-4}
3	multilayer film[b]	6 bilayers	0.2589	390[f]	0.11	2.55	9.945×10^{-6}	2.141×10^{8}	5.170×10^{-5}
4		12 bilayers	0.5625	847[e]	0.18	2.55	2.160×10^{-6}	2.228×10^{8}	3.741×10^{-5}
5	spin-coated film[c]			914[g]	0.10	2.60	2.093×10^{-6}	2.099×10^{8}	2.211×10^{-5}

[a] Multilayer film of *H*-PURET and Eu(III), pH 6.5 (*H*-PURET), 7.0 (Eu^{3+}). [b] Multilayer film of *H*-PURET and PDAC, pH 5.5 (*H*-PURET), 7.5 (PDAC). [c] Spin-coated film of 5% *H*-PURET solution in DMF/PGMEA (80/20) at 1000 rpm for 65 s. (DMF-dimethylformamide; PGMEA-propylene glycol methyl ether acetate). [d] Absorbance at 419 nm (1 and 2), at 462 nm (3 and 4). [e] Determined by Atomic Force Microscopy (AFM). [f] Calculated by eq 2. [g] Measured by Auto EL ellipsometer (Rudolph Research). [h] Calculated by eq 1.



(a) (b)

Figure 6. Electroluminescence characteristics under forward bias condition. (a) Spin-coated film of polymer (*H*-PURET); (b) Multilayer (20 bilayers) film. (ITO/polyaniline/emitting layer/Al).

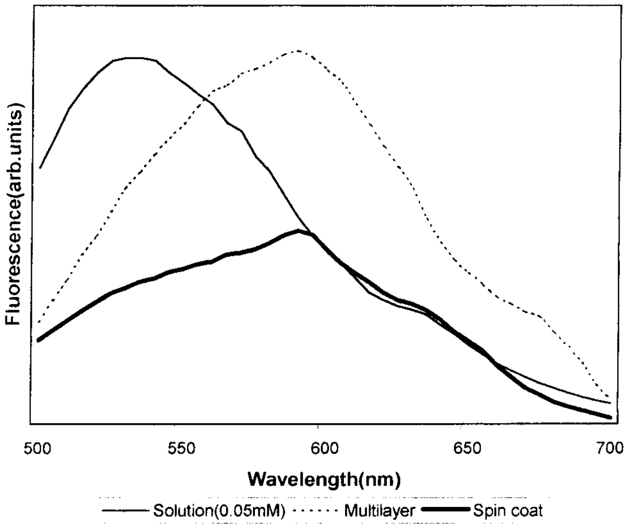


Figure 7. Fluorescence behavior of solution and spin-coated film of *H*-PURET to compare the fluorescence of multilayer *H*-PURET/Eu(III) complex film. Solution: 0.05 mM, pH 7.5, λ_{ex}: 384 nm, $\lambda_{em,\ max}$: 528 nm; spin-coated film: 680 Å on slide glass λ_{ex}: 389 nm, $\lambda_{em,\ max}$: 590 nm; multilayer film: 20 bilayers on slide glass λ_{ex}: 387 nm, $\lambda_{em,\ max}$: 591 nm.

Photoluminescence spectra of the spin-coated and polymer–europium complex multilayer films show that the contribution of europium complex to the fluorescence of the multilayer film is small when it is excited at 387 nm. A part of the luminescence peak from the multilayer at around 610 nm increased slightly compared to the same spectral region of the spin-coated film; the fluorescence signal resulting from the europium complex seems to be merged with the broad emission band of *H*-PURET. The small contribution in emission due to the complex could be explained based on the very small absorption of the complex at the excitation wavelength.

On the other hand, we observed a significant contribution from the europium complexes to the EL intensity of the multilayer film (Figure 6). The observed EL output powers of multilayer films are about 2 times higher those of spin-coated films alone. This enhancement can be explained in terms of the added EL from the europium complex.

Although carboxyl groups are well-known bidentate ligands,[48] the luminescence from the complexes with metal ions is weak. Highly enhanced electroluminescence in metal–ion complexes can be achieved when effective energy transfer from excited ligand molecules to the metal ions takes place [ligand-to-metal energy transfer (LMET)].[40,49–50] We have demonstrated this by observing highly enhanced (up to 20 times) EL signals by doping the PURET polymer with small amounts of *tris* (4,4,4-trifluoro-1-(2′-thienyl)-1,3-butanedionato-O,O′) europium (III) hydrate ($Eu(ttfa)_3$) complex. The 4,4,4-trifluoro-1-(2′-thienyl)-1,3-butanedione ligand is known to effectively transfer energy to metal ions (Figure 8).[51] Polyaniline and 8-hydroxyquinoline aluminum salt (Alq_3)[52,53] were used as hole and electron

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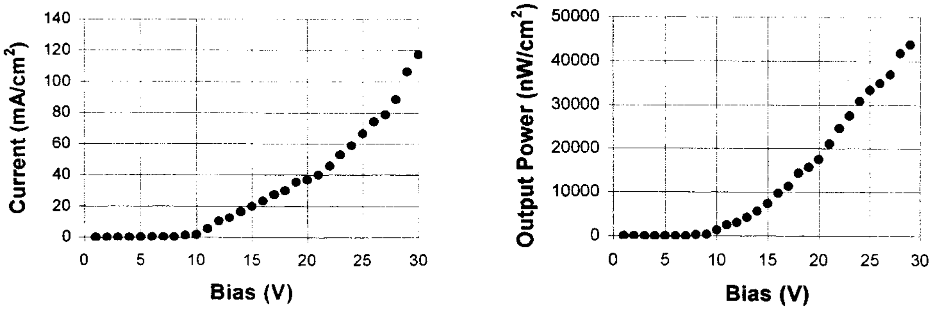

Figure 8. Electroluminescence characteristics of blends of PURET and Eu(ttfa)$_3$ complex under forward bias condition. (ITO/polyaniline/PURET-1% Eu(ttfa)$_3$/Alq$_3$/Al).

transfer layer, respectively, in this experiment.

The comparison of device currents of spin-coated and multilayer film-based LEDs indicated that multilayer films are more conductive than spin-coated films by about a factor of 4. This is consistent with the results from the conductivity measurement (Table 1).

4. Conclusion

We have successfully developed a new technique to fabricate multilayers of *H*-PURET-Eu^{3+} complexes employing a layer-by-layer complexation deposition approach by alternatively dipping desired substrates in aqueous *H*-PURET and EuCl$_3$ solutions. FT−IR spectra and EDXS spectra indicate the presence of coordination bonding between carboxalate ligands and Eu^{3+} ions. The conductivity of the multilayer film was an order of magnitude higher than that of the spin-coated film. Electroluminescence (EL) brightness of the fabricated device employing multilayer films was about twice that of the spin-coated film from the pure polymer solution.

This new type of layer-by-layer deposition technique has several noticeable advantages, including the ability to control thickness at the molecular level, adaptability of the fabrication process to large-area substrates, and deposition of insoluble metal−polymer complexes as uniform thin films. Because in principle, multilayer films can be prepared through various combinations of metal-macromolecular ligands, this technique can be extended to fabricate a stack of multilayers containing different types of metal complexes for optical and electronic applications.

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