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Preparation of Oriented Ultrathin Films via Self-Assembly Based on Charge Transfer Interaction between π-Conjugated Poly(dithiafulvene) and Acceptor Polymer

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Introduction. Self-assembled ultrathin multilayer films have been intensively investigated in recent years since Decher et al. introduced the method for preparing multilayer ultrathin films by the consecutive deposition of oppositely charged polyelectrolytes from dilute aqueous solution onto charged substrates.[1,2] Forces between the layers are primarily electrostatic and covalent bonds, but they can also involve hydrogen bonding and $\pi-\pi$ interaction. Charge transfer (CT) interaction as the driven force of layer-by-layer self-assembled ultrathin films was investigated for the first time by Ito et al.[3−6] In their work a new concept was established for the fabrication of multilayer films by consecutively alternating adsorption of two kinds of nonionic polymers, both of which have electron-donating or -accepting groups at the side chains.

Recently, layer-by-layer self-assembled membranes from conjugated polymers have been prepared with the aid of electrostatic interaction,[7−10] hydrogen bonding,[11] or acid−base reaction[12] for potential applications in chemical sensors, transparent electrodes for light-emitting devices, and other molecular devices. However, conductive ultrathin films via self-assembly based on CT interaction have not been reported. Novel π-conjugated poly(dithiafulvene) (PDF) containing strong electron-donating dithiafulvene (DF) units in the main chains were recently synthesized by our group.[13] Two kinds of CT complexes of PDF with 7,7,8,8-tetracyanoquinodimethane,[14,15] or viologen derivatives,[16] were presented to reveal the strong electron-donating property of PDF. The DF units with electron-donating property in PDF backbones are involved in the CT interaction, and electron delocalization spread through the whole main chains of the oxidized π-conjugated PDF. These results motivated us to apply CT interaction between PDF and a viologen polymer as an acceptor polymer to prepare self-assembled multilayer ultrathin films as depicted in Figure 1.

In this communication, we report the new layer-by-layer manipulation of PDF and the viologen polymer by CT interaction and their unique physical properties. The layer-by-layer self-assembled ultrathin film was prepared via consecutively alternating immersion of substrates into dilute dimethyl sulfoxide (DMSO) solutions of PDF and poly(hexanyl viologen) (6-VP). The charge transfer (CT) interaction formed at solid−liquid interfaces between the polymer backbones of PDF and 6-VP was employed as the driven force of the alternative deposition of the multilayer ultrathin film.

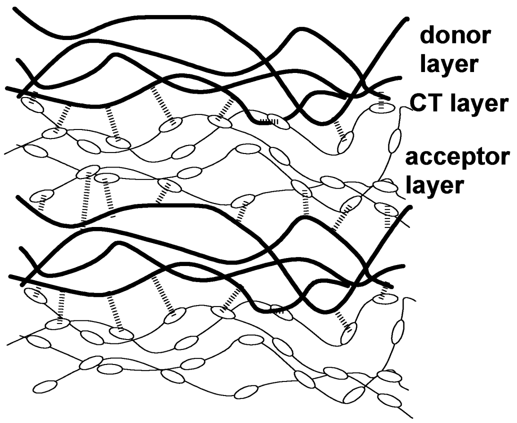
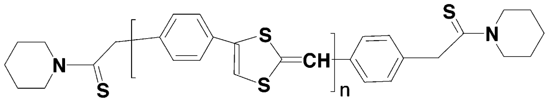
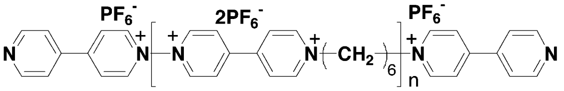


Figure 1. Schematic diagram of the layer-by-layer network of a self-assembled multilayer film. The polymer backbones of the π-conjugated electron donor are simplified into bold curves, and the beadlike units on the thin curves represent the electron acceptor sections in acceptor backbones. CT complexes formed between the electron donor and the acceptor are depicted with broken lines. One layer of the electron donor and one layer of the electron acceptor are called one bilayer in this work.

Chart 1



Poly(dithiafulvene) (PDF)



Poly(hexanyl viologen) (6-VP)

Experimental Section. Poly(dithiafulvene) (PDF) (M_n = 3400 by ^{1}H NMR) was prepared by the cycloaddition polymerization of aldothioketene with its alkynethiol tautomer derived from 1,4-diethynylbenzene as reported before.[14,15] Poly(hexanyl viologen) (6-VP) (M_n = 2400 by ^{1}H NMR) was synthesized from 1,6-dibromohexane and 4,4′-bipyridyl as reported,[17] and its counterions were transformed to hexafluorophosphate (PF_6^-). The chemical structures of PDF and 6-VP are shown in Chart 1. Indium-doped tin oxide (ITO) glass substrates were washed with *n*-hexane for three times and then sonicated in concentrated nitric acid for 30 min and finally cleaned with methanol for three times and dried overnight in an oven at 100 °C. The clean ITO substrate was immersed into 5 wt % aqueous solution of poly(diallyldimethylammonium chloride) for 30 min to introduce positive charges onto the substrate surface[12] and was washed with a large amount of distilled water to remove excessive cationic polymers and dried completely in a vacuum. This step was repeated again to improve the adsorption of the cationic polymer. Then the substrate was immersed into 1 wt % aqueous solution of poly(sodium 4-styrenesulfonate) (PSSNa) for 30 min to induce stable charge reversal[9,18] and was washed with

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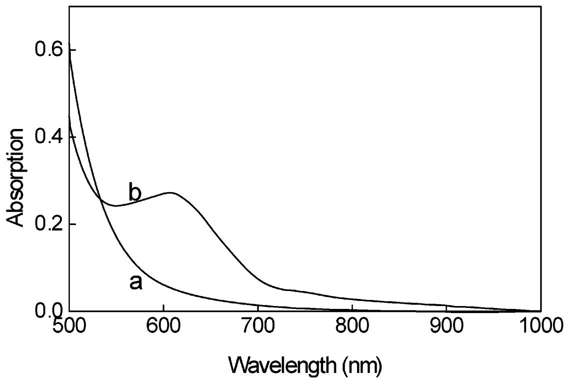

Figure 2. UV−vis absorption spectra for the PDF solution in DMSO (a) before and (b) after the addition of methyl viologen dihexafluorophosphate.

a large amount of distilled water and dried in a vacuum. The adsorbed polymers on the insulated side of the ITO substrate were wiped off by Kimwipes wipers with water and then DMSO to prevent the insulated side from adsorbing the polymers. The ITO slide with negatively charged surface was used as the substrate for the adsorption of the first layer of 6-VP. The preparation of the layer-by-layer self-assembled ultrathin film by CT interaction was carried out as follows. The substrate was immersed in a 1 wt % DMSO solution of 6-VP for 20 min and washed with DMSO carefully to remove excessive 6-VP. After being dried in a vacuum, the substrate was dipped into 0.5 wt % DMSO solution of PDF for 15 min. The washing and drying steps were the same as the last adsorption step of 6-VP. The immersion step of PDF was repeated again to ensure a complete adsorption of PDF. In fact, adsorption of PDF was hardly recognized after the second dipping process compared with the first dipping by UV−vis absorption measurement. Multilayer films were obtained by repeating the alternating immersion steps in 6-VP and PDF solutions as described above.

UV−vis absorption spectra of the mixed solutions and the multilayer films were recorded using a Jasco-530 spectrophotometer. Backgrounds of the negatively modified substrates were subtracted from all spectra of the multilayer films. Oriented electrical conductivities of the multilayer films were measured at room temperature by a two-probe technique using a Keithley model 236 source measurement unit. For the conductivity in the direction along the film surface, two thin Pt wire leads were contacted at the surface of the film with carbon paste. For the perpendicular conductivity, one Pt wire lead was contacted at the surface of the film and the other Pt wire lead was contacted at the unmodified area of the ITO glass surface.

Results and Discussion. The UV−vis absorption spectrum for the DMSO solution of PDF and methyl viologen dihexafluorophosphate as an electron-accepting unit of 6-VP shows a characteristic CT absorption band at around 600 nm (Figure 2). An admixture of PDF and 6-VP in DMSO also produced a greenish solution instantaneously, indicating CT complex formation in the solution. Green precipitation was observed in the mixed solutions after these solutions were kept for more than 12 h. The ESR spectrum of the precipitate consisted of two types of signals. A sharp signal ($g = 2.005$) was assigned to the anion radical of the viologen unit.[19] A broad singlet line ($g = 2.011$) is almost the same as that of the ESR signal of the TTF−TCNQ complex.[14] These results indicate the CT complex formation of PDF with 6-VP.

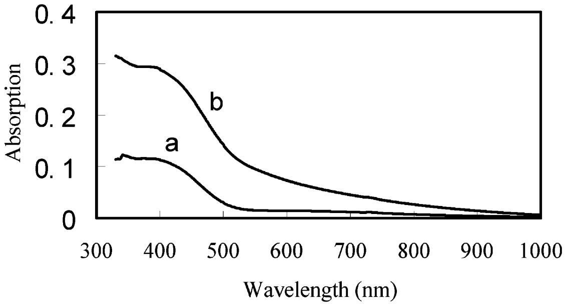

Figure 3. Absorption spectra of (a) two bilayers and (b) eight bilayers deposited on the negatively modified ITO glass substrate.

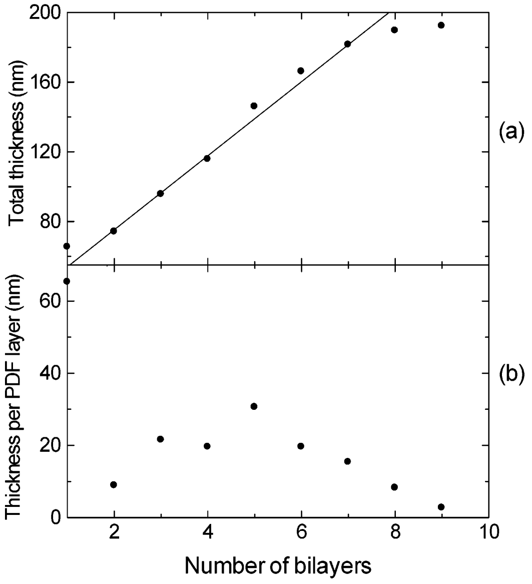

Figure 4. Dependence of (a) total thickness and (b) thickness per PDF layer on the number of bilayers. The PDF layer thickness was estimated from UV−vis spectra at 389 nm.

The UV−vis absorption spectra of two bilayers and eight bilayers of PDF and 6-VP deposited onto the ITO glass substrate are presented in Figure 3. The absorption below 550 nm is mainly from the accumulative absorption of PDF and 6-VP, and the broad absorption band up to 1000 nm increased bilyer-by-bilayer, which indicates the formation of CT complex at the solid−liquid interfaces between the electron donor and acceptor polymers. CT interaction between donor and acceptor layers was the driven force of the layer-by-layer self-assembly.

In a controlled experiment, we tried to deposit a PDF layer onto the modified ITO glass substrate without introducing the 6-VP layer. From UV−vis analysis, no PDF was adsorbed on the modified substrate. The bare ITO glass also prevented the adsorption of PDF. These results proved that the CT interaction is essential for the preparation of the layer-by-layer films in the present system.

The total thickness increase from the one bilayer to the nine bilayers of 6-VP and PDF and the thickness of each PDF layer are shown in Figure 4. The molar absorption coefficient at 389 nm of the DF unit in PDF ($\epsilon = 3.28 \times 10^{3}$ M^{-1} cm^{-1}) was used for calculation of the PDF layer thickness, assuming that the density of the bulk film is 1.0 g/cm^3. The thickness of the first PDF layer was 3 times that of the others. This behavior can be explained by larger amounts of 6-VP adsorption on the negatively charged substrate than that on PDF layers. A linear relationship was observed between absorption and the number of deposited bilayers until seven bilayers, which indicates that the deposition process in all cases is reproducible from layer to layer. The average thickness of each PDF layer except the first PDF layer is 24 nm. Relatively thicker layers might be produced by the existence of a greater fraction of PDF segments in loops and tails due to lower levels of intrasegmental repulsion of PDF.[20] Termination of growth after eight layers was observed, which may be due to the relatively weak interaction between the donor and acceptor polymers.

Oriented electrical conductivity measurement of the nine-bilayer film provided that the electrical conductivity was 1.4×10^{-5} S cm^{-1} in the direction perpendicular to the film surface. However, the conductivity rose to 3.8×10^{-3} S cm^{-1} in the direction along the film surface, more than 2 orders of magnitude greater than that in the direction perpendicular to the film surface. This electrical anisotropy indicated the formation of the layer-by-layer heterostructure multilayer film. The layer-by-layer heterostructure in the multilayer film was further supported by cyclic voltammogram (CV) measurements. A series of the layer-by-layer films on the ITO glass substrates of 1, 2, 3, 4, 5, and 8 bilayers exhibited no oxidation peaks, while a cast film of PDF on a bare ITO glass showed an oxidation peak at 0.6 V vs Ag/AgCl. This result is consistent with the electrical properties of the multilayer films. In the direction perpendicular to the film surface, electron transfer becomes difficult compared with that in the direction along the film surface due to the sandwich structure of the multilayer films.

Conclusions. The layer-by-layer self-assembled ultrathin films with controlled thickness were successfully prepared via the adoption of a simple approach of immersing the modified ITO glass substrate in 6-VP and PDF solutions alternatively. The UV−vis absorption spectra ensured that the CT complex was formed between the polymer backbones of the electron acceptor and the donor in the ultrathin films at the liquid−solid interfaces. Electrical and electrochemical measurements were carried out for the multilayer ultrathin films. The electrical conductivity changed by more than 2 orders of magnitude in the directions along and perpendicular to the surface of the multilayer film. No peak associated with the oxidation of PDF appeared in the cyclic voltammogram for multilayer films as a result of the heterostructures of the multilayer films.

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