Energy Transfer in Poly(3-thiopheneacetic acid) and Oligothiophene Polyelectrolyte–Surfactant Complexes

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Introduction

Ir-conjugated oligothiophenes and polythiophenes have drawn much interest due to their promising applications in organic transistors, light-emitting diodes (LEDs), and other semiconductor and display devices.1–7 Various types of substituted oligothiophene and polythiophene derivatives have been synthesized and characterized in order to achieve liquid-phase processability.8–10 In our previous studies, terthiophene and sexithiophene amphiphilic surfactants were synthesized and used for the preparation of gold nanoparticles and layer-by-layer self-assembled ultrathin films with potential applications as organic field-effect transistors (FETs).11,12 Langmuir–Blodgett films have also been prepared from α,ω-diamine oligothiophene amphiphilic surfactants.13

Recently, Botta et al. reported that energy transfer (ET) could take place from a higher energy terthiophene to a lower energy quinque thiophene in perhydrotriphenylenes (based on HOMO and LUMO matching).14 ET is a process in which excitation energy is released from one species to another in various environments.15 In α-conjugated molecular and polymeric systems, ET processes and their dynamics have been extensively studied for their optoelectronic applications.17–19 Especially, in organic LEDs, an efficient color conversion technique based on ET can be used to convert their emission color to longer wavelengths via a simple blending method of conjugated polymers. Also recently, Lee et al. reported that energy could be transferred from pendant oxadiazole sidegroups to conjugated main chains, poly(phenylene vinylene) (PPVs), to a certain extent.20 In this study, we report an interesting and efficient ET process within a polyelectrolyte–surfactant complex (PSC) of an oligothiophene amphiphilic surfactant, 5-(6-trimethylaminohexyl)-2,2′:5′,2′′-terthiophene (AHTT), and poly(3-thiopheneacetic acid) (PTAA) that has a conducive environment for ET to take place. We have observed that up to 42 mol % of the anionic groups in PTAA can be complexed with the positively charged AHTT that is partially soluble in water at room temperature. The ET efficiency is related to the overlap of the PTAA absorption spectrum with the emission spectrum of AHTT, the distance between the two species, and the composition of the PSC.

Figure 1. Chemical structures of the thiophene based polyelectrolyte surfactant complexes of AHTT and PTAA.

Experimental Section

Materials. All the essential chemicals and reagents were purchased from Aldrich, and all of the reactions were carried out under nitrogen atmosphere. Deionized water used in all experiments was purified with an ion-exchange and filtration unit (Milli-Q Academic System, Millipore) equipped with a 0.22 µm Millistack filter at the outlet. The resistivity was 18.2 MΩ•cm. Figure 1 shows the chemical structures of AHTT and PTAA used in this study. AHTT was obtained by an amination reaction (quaternary amine formation) of 5-(6-bromohexyl)-2,2′:5′,2′′-terthiophene (BHTT), by stirring with an excess of trimethyloxilamine in methanol solution for 60 h. The synthesis of BHTT was reported in our previous study in detail.21 PTAA was synthesized by the oxidative polymerization of ethyl-3-thiopheneacetic acid with anhydrous ferric chloride in chloroform, followed by treatment with 1.5 equivalents of 6-(trimethylamino)hexyl chloride hydrochloride in anhydrous pyridine. The polydispersity index was 1.7.

by acid hydrolysis of the ester group.\textsuperscript{22–24} The PTAA was dissolved in a 0.01 M NaOH solution at a concentration of 1 mg/mL, and then various amounts of AHTT were dissolved in the PTAA solution. AHTT alone is partially soluble in water at room temperature but forms a very soluble PSC with PTAA. These PSCs of AHTT in the PTAA solution were used to observe ET between oligothiophene and polythiophene as a function of excitation wavelength and composition.

**Spectroscopic Measurements.** The UV–vis spectra were obtained using a Perkin-Elmer spectrophotometer (Lambda 20) in a quartz cuvette. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer spectrofluorometer (LS50B) equipped with a Xenon lamp using a quartz cell.

**Results and Discussion**

Figure 2 shows UV–vis absorption and PL emission spectra of AHTT and PTAA. PL emission spectra of AHTT and PTAA were obtained after excitation at 360 and 420 nm, respectively. As can be seen, the PL emission spectrum of AHTT overlaps the UV–vis absorption spectrum of PTAA. Spectral overlap between the absorption of the acceptor and the emission of the donor and their proper spacing are required for efficient Förster-type ET.\textsuperscript{25}

In our previous study, it was found that AHTT dissolves well with a solution of poly(sodium 4-styrenesulfonate) (PSS).\textsuperscript{12} The improved solubility of AHTT was due to the formation of a polyelectrolyte complex with PSS. The complexation is driven by the electrostatic attraction between the two species. AHTT also dissolves well in a solution of PTAA. Up to 42 mol % of the anionic groups in PTAA could be complexed to AHTT without precipitation of the PSC. Figure 3 shows UV–vis absorption spectra of polyelectrolyte–surfactant complex solutions with different concentrations of AHTT. The main absorption band observed around 360 nm is attributed to the terthiophene units in the PSC solution, which was also observed in the absorbance spectra of a PSS solution where 40 mol % of the anionic groups were complexed with AHTT.\textsuperscript{12} This absorption band showed a linear increase with increased concentration of AHTT, indicating anionic groups in PTAA were well complexed to AHTT.

Figure 4 shows PL emission spectra of PTAA solutions with different concentrations of AHTT upon photoexcitation at 360 nm. The PL emission spectra of PTAA ($\lambda_{\text{exc}} = 360$ nm) were observed for all PSC solutions, and their intensities were enhanced with increased content of AHTT up to 33 mol %. At 42 mol % of AHTT, the PL intensity decreased slightly, possibly due to an inner filter effect.\textsuperscript{27,28}


\textsuperscript{25} Förster, T. Ann. Phys. 1948, 2, 55.


Also, PL emission spectra of AHTT ($\lambda_{\text{max}} = 420 \text{ nm}$) in the PSC solutions were clearly detected only for 42 mol % AHTT. Therefore, it is concluded that the enhancement of the PL emission intensity of PTAA in the PSC solutions is attributed to ET from AHTT excitations to PTAA, and it was very efficient. Furthermore, 33 mol % gave the optimum PL behavior, which did not necessarily coincide with the maximum stoichiometry for complexation without precipitation.

Chen et al. reported dramatic emission enhancement of poly(2,5-methoxypropyloxysulfonate phenylene vinylene) (MPS-PPV) simply by adding a small amount of cationic surfactant, dodecytrimethylammonium bromide, due to the reduction of conformational disorder of MPS-PPV. The electrostatic repulsions between carboxyl groups of PTAA can be affected by adding AHTT, and its conformation can also be changed, leading to a modification of conjugation length. However, the emission spectra of the PSC solutions were independent of the excitation wavelength (from 300 to 450 nm), and emission maxima of PTAA were not shifted, although there was an emission enhancement with increasing AHTT concentration. This indicates that the conformation of PTAA was not affected significantly enough to shift the emission maximum by AHTT complexation. The inner filter effect correlates to the optimum PL observed at 33 mol %, which indicates that, at 44 mol %, partial aggregation or reabsorption tends to decrease the quantum efficiency. Note again that precipitation of the complex occurs beyond 44 mol %.

In conclusion, a PSC may be formed between PTAA and AHTT in which efficient energy transfer is observed. Up to 42 mol % of the anionic groups in PTAA can be complexed with AHTT. PL emission spectra ($\lambda_{\text{max}} = 545 \text{ nm}$) of PTAA were observed for all PSC solutions (concentrations) upon photoexcitation at 360 nm, and their PL emission intensities were enhanced with increasing AHTT content. The enhancement of PL emission can be attributed to the direct energy transfer from AHTT excitations to PTAA, and it was found to be very efficient. The emission spectra of the PSC solutions were independent of the excitation wavelength. The emission maxima were not shifted, indicating that the conformation of PTAA was not significantly affected by AHTT surfactant complexation even at different compositions.

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