

Photothermally Induced Conformational Changes in Poly(Substituted Thiophene) Film Leading to Nanometer Surface Protrusion: A Near-Field Fluorescence Microspectroscopic Study

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The relationship between changes of fluorescence spectrum, polymer conformation, and surface morphology of a poly{3-[2-(*N*-dodecylcarbamoxyloxy)ethyl]thiophene- 2,5-diyl} (P3DDUT) film were examined by near-field fluorescence microspectroscopy. By a 488 nm excitation using the near-field probe, a nanometer scale protuberance was formed on the surface. The excitation also induced a blue shift in the fluorescence spectrum. By analyzing the spectral change, it was confirmed that photothermally induced conformational changes (rod-coil transformations) lead to the nanometer surface protrusion. Moreover, in exposure time dependence measurements, it was found a time lag in appearances of the blue shift and the protrusion, indicating that an accumulation of transformed polymers is necessary to evolve into the surface protrusion.

Introduction

Near-field scanning optical microscopy (NSOM) has been proved a powerful tool for investigating optical properties with a spatial resolution up to subwavelength.¹ By combining NSOM with conventional spectroscopic techniques such as fluorescence, Raman, infrared absorption, and light scattering spectroscopies, photophysical and photochemical properties in small domains have been revealed.² Most of the reports by the near-field microspectroscopy deal only with the physical and the chemical nature of target materials, whereas the microspectroscopy has another advantage, which is the simultaneous measurement of surface morphology and spectroscopic properties through the shear-force technique. The advantage enables us to analyze the microspectroscopic properties as a function of the height/thickness or the surface morphology of a sample, which can be never attained by the use of other techniques such as confocal or multiphoton microspectroscopy. However, there are few near-field microspectroscopic studies elucidating the relationship between the microspectroscopic properties and topographic features as far as we know.³

So far, we have revealed by the use of the picosecond near-field microspectroscopy system⁴ that, in some organic materials, characteristic optical properties are closely related to topographic features.^{5,6} For example, it was demonstrated for individual tetracene single microcrystals that defects giving an excimer emission are less for a thinner area; that is, a thinner crystal is more ideal with respect to the crystal structure.⁵ In our previous study of a P3DDUT film (see Figure 1a for the chemical structure), we have shown that fluorescence spectra at protruding domains were slightly blue-shifted compared with flat areas, and a further blue shift could be induced more appreciably by

a long time excitation.⁶ It is well-known that fluorescence properties of P3DDUT are determined by its conformations in films.⁷ Consequently, it was concluded that in the protruding domain major polymers take a disordered conformation, in which there are some distortions in the main chain decreasing the conjugation length and interchain interactions are rather weak, whereas an ordered conformation giving a longer conjugation is favored in the flat area. Thus, it has been revealed that there is a direct correlation between local fluorescence properties, molecular conformations, and surface morphologies in the P3DDUT film.

In addition, we have found that the polymer conformation in the P3DDUT film can be modified by a near-field excitation. Thus, it is expected now that the conformational change may affect the surface morphology, which is examined for a P3DDUT film by use of the near-field fluorescence microspectroscopy. We demonstrate that a surface protrusion can be induced by a near-field excitation accompanied with a spectral blue shift and consider that the behavior results from photothermally induced conformational changes. In addition, the time evolution of polymer conformational and surface morphological changes are presented and discussed.

Experimental Section

P3DDUT was synthesized as reported previously.^{7b} P3DDUT was dissolved in chloroform (Nacalai Tesque, Spectro-Grade, without further purification) with 0.25 wt %. For removing dusts and aggregated polymer particles, the solution was filtered through a membrane filter with a pore size of 200 nm. Glass coverslips were washed with a detergent solution and immersed in pure water with sonication for 1 h. A film was prepared from the chloroform solution by spin-coating onto the glass coverslip at 1000 rpm for 60 s, and then the solvent was evaporated. The film thickness was approximately 80 nm.

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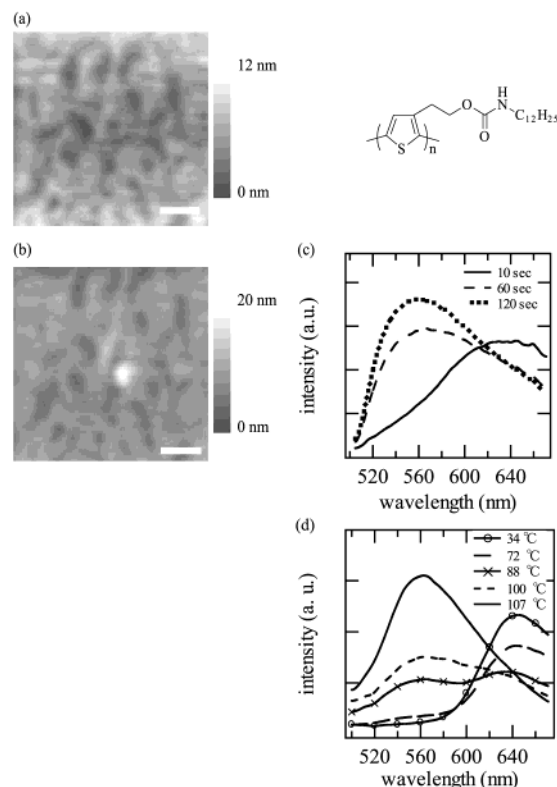


Figure 1. (a) Shear-force image of the pristine P3DDUT film (left) and the chemical structure of P3DDUT (right). The scale bar indicates 1 μm . (b) Shear-force image of the P3DDUT film after excitation. Excitation wavelength and exposure time are 488 nm and 2 min, respectively. The scale bar indicates 1 μm . (c) Fluorescence spectra obtained at the protruding area in b. Representative spectra at three selected times under a continuous excitation are shown. Each spectrum is accumulated for 1 s. (d) Temperature-dependent fluorescence spectra of the P3DDUT film measured by a conventional spectrofluorometer with a ceramic heater.

The details of our near-field fluorescence microspectroscopy system were reported elsewhere.⁴ For preparing a NSOM probe, an optical-fiber was tapered by a fiber puller (Sutter, model P2000) and aluminum-coated by an evaporator with a fiber-rotating mechanism in a high-vacuum chamber. The aperture size of the probe was ~ 100 nm. NSOM probe was scanned across the sample, keeping the probe-sample distance within ~ 10 nm through the shear-force feedback. The 488 nm light from an argon ion laser (Omnichrome, 543-AP) was coupled into the NSOM probe with the power of <1 mW. The light was emitted from a small aperture at the end of the NSOM probe and excited the film. Fluorescence from the sample was collected with a microscope objective (40 \times , 0.65 N. A., Olympus, ACH40X). The collected light was passing through a colored glass filter which transmits only emission signals longer than 520 nm, thus blocking the excitation light. For fluorescence imaging, the remaining fluorescence was detected by an avalanche photodiode (EG&G, SPCM-AQ) with 550 or 650 nm band-pass filters (± 40 nm). On the other hand, the local fluorescence spectrum was measured with a polychromator (Jasco, CT-10) and a liquid-nitrogen-cooled CCD camera (Photometrics, SDS 9000). All of these experiments were conducted in air at room temperature.

Temperature dependence of fluorescence spectra of the film was measured by a conventional spectrofluorometer (HITACHI, F4500) with a ceramic heater.

Results and Discussion

Figure 1a shows the shear-force topographical image of the pristine P3DDUT film. Although the surface seemed slightly bumpy, the surface roughness was smaller than 3 nm, and there was no topographic feature larger than several hundreds nanometers in width. A small spot was excited with the 488 nm light by fixing the NSOM probe at a center point in Figure 1a, and as a result, a protuberance with a 15 nm height and a 280 nm width was formed as shown in Figure 1b. The laser power coupled into the NSOM probe and the exposure time were 1 mW and 2 min, respectively. It is interesting to note that the surface protrusion was accompanied with a fluorescence spectral change. Figure 1c shows fluorescence spectra detected at the excited point in Figure 1b. These are representative spectra at three selected times under a continuous excitation. Upon excitation, a peak at 640 nm decreases, whereas a new peak appears at 560 nm. The obtained protuberance and the blue-shifted fluorescence spectrum were maintained at least for 1 h.

It is well documented that, upon excitation, fluorescence spectra of conjugated polymer films can be easily modified because of photooxidation, producing carbonyl groups which decrease conjugated lengths.⁸ These carbonyl defects also act as nonradiative center for excitons, quenching whole wavelength components of fluorescence. In our case, however, fluorescence spectra showed brightening short wavelength components (blue shift). It is unlikely that a photooxidation is solely responsible for the blue shift. Conformational changes, decreasing the conjugation length, should be considered as the origin of the blue shift. It is well-known that the fluorescence spectrum of P3DDUT and other poly(substituted thiophene) films show blue shifts upon heating, which are caused by conformational changes of polymer chains such as rod-coil transformations in films.^{6,9} Figure 1d shows temperature-dependent fluorescence spectra measured by a conventional spectrofluorometer. The excitation wavelength was 475 nm. As the temperature rose, the peak at 640 nm decreased, whereas a new peak appeared at 560 nm. In the present NSOM experiments, photoexcitation resulted in the fluorescence spectral change, whose tendency was qualitatively similar to the thermal effect on fluorescence spectra. Therefore, it is considered that a rod-coil transformation is also induced by near-field excitation. In this case, it is likely that the conformational change is induced photothermally. We consider the mechanism as follows. Before excitation, polymer chains take a rodlike conformation, in which adjacent thiophene rings are coplanar and thus their conjugation length is long. Because the fluorescence of P3DDUT film is not intense, i.e., its radiationless transition yield is high,¹⁰ the excitation energy is converted to molecular and lattice vibrational energy and temperature elevates effectively. As the temperature rises, polymer chains may tend to twist and adopt a coillike conformation. Because at the twisting points the conjugation is interrupted, conjugation length becomes shorter and fluorescence spectrum is blue-shifted.

Next, we consider the origin of the surface protrusion. As mentioned above, the surface protrusion by near-field excitation was accompanied with a spectral change because of a rod-coil transformation. The temperature dependence of the X-ray diffraction has revealed that the molecular volume and the interchain distances increase because of rod-coil transformation.^{7b,9c,11} It is likely that the expansions in the interchain space evolve into a surface protrusion. Therefore, it is concluded that the surface protrusion accompanying the blue shift in the fluorescence spectrum results from photothermal rod-coil transformations.

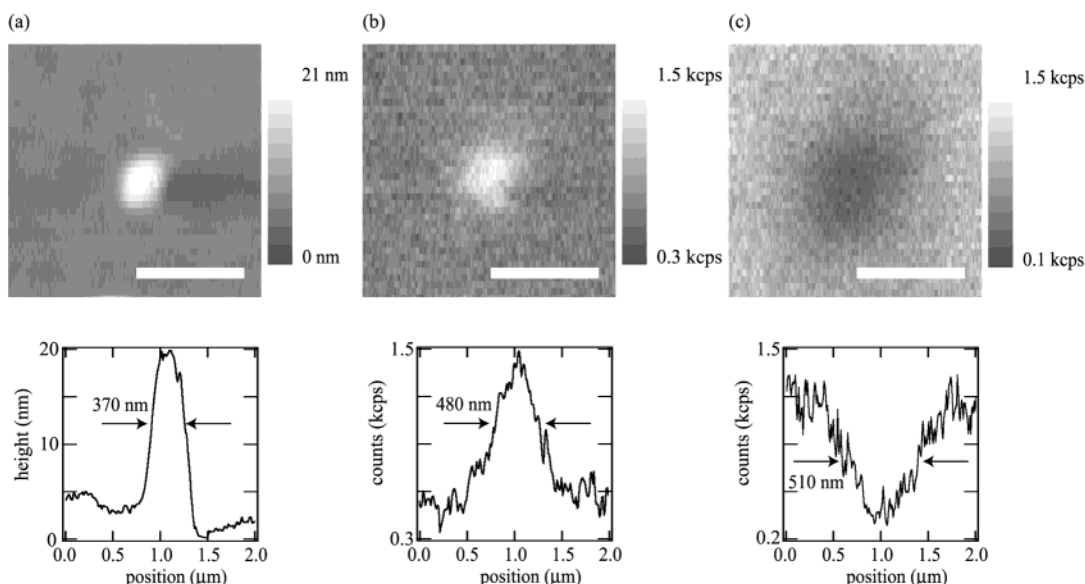


Figure 2. (a) Shear-force and (b and c) fluorescence images (top) and their corresponding cross sections (bottom) of the P3DDUT film after excitation. Excitation wavelength was 488 nm. The laser power coupled into the NSOM probe was 0.5 mW and the exposure time was 2 min, respectively. Detection wavelengths in b and c are 550 ± 40 nm (fluorescence of coillike polymers) and 650 ± 40 nm (fluorescence of rodlike polymers), respectively. The scale bars indicate $1 \mu\text{m}$.

One may doubt our statement saying that the photothermal effect is the only origin of the conformational change. Because it is well-known that the end of the NSOM probe is considerably heated because of photoabsorption by aluminum coating,¹² it may induce the conformational changes and generate the surface protrusion. To investigate the above contribution, we have conducted the same experiments except using a 633 nm light from a He–Ne laser with 1 mW, which is hardly absorbed by P3DDUT.^{7b} We could not reproduce the conformational changes and the protrusion observed above, indicating that a direct heating effect by the hot probe is not effective.

The relationship between the protrusion and the spectral blue shift due to a rod–coil transformation can also be confirmed by shear-force and fluorescence images as shown in Figure 2. Detection wavelengths in Figure 2 parts b and c were 550 ± 40 nm (fluorescence of coillike polymers) and 650 ± 40 nm (fluorescence of rodlike polymers), respectively. Corresponding to the rod–coil transformation, a bright spot (Figure 2b) and a dark one (Figure 2c) were formed. The width of the protuberance, the bright spot and the dark one was 370, 480, and 510 nm, respectively, which were wider than the irradiation spot estimated from the aperture size of the NSOM probe. It is unlikely that the broadening results from an excitation by the large aperture probe, since we have confirmed that the effective aperture diameter still remains 150 nm by a measurement of the chromium checkerboard after all of the experiments (not shown). These broadenings may be due to a thermal diffusion, inducing a rod–coil transformation in nonirradiated areas. Moreover, it is interesting to note that the width of the protuberance was narrower than that of the bright and dark spots.

An exposure time dependence provides a detailed relationship between the surface protrusion and polymer conformational changes. Shear-force and fluorescence images in Figure 3 show arrays of some protuberances and bright spots formed with various exposure times. With increasing exposure time, the protuberance and the bright spot became higher and brighter, respectively. Also the width of the protuberance and the spot became larger. The growth of the protuberance saturated to ~ 30 nm in height with 8 min exposure. It is important to note that the times for the appearance of the protuberance and the bright

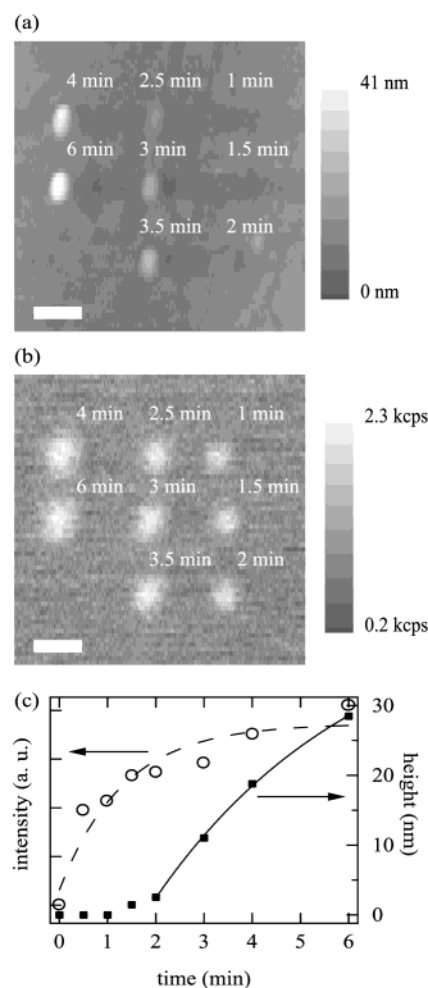


Figure 3. (a) Shear-force and (b) fluorescence images of the P3DDUT film showing protuberances and bright spots formed with various exposure times as given in the figures. The laser power coupled into the NSOM probe was kept with 0.3 mW. Detection wavelength in b is 550 ± 40 nm (fluorescence of coillike polymers). The scale bars indicate $1 \mu\text{m}$. (c) Time evolution in the height of each protuberance (closed squares) and its fluorescence intensity (open circles).

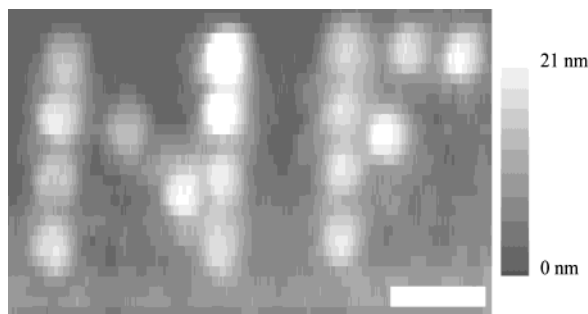


Figure 4. Shear-force image of patterned protuberances, as letters “N” and “F”. Each point was excited for 2 min and their spacing was 600 nm. The scale bar indicates 1 μm .

spot do not correspond with each other. Figure 3c shows heights of the protuberances (closed squares) and peak intensities of bright spots (open circles) as a function of the time exposure. Each data point is the average of three measurements. The time evolution of the fluorescence intensities indicates that coil-like polymers were formed by short exposure and then increased. On the other hand, the surface showed hardly the protrusion during the first 2 min. By a prolonged excitation, the amount of coiled polymers increased furthermore and then the protuberance at last started to grow larger. These results indicate that an accumulation of coil-like polymers above a certain critical density is necessary for the appearance of the surface protrusion. In general, polymer films have a large free volume. Because the amount of the coiled polymer is small in the early period of the excitation, the increase in the molecular volume due to a rod-coil transformation may be compensated by the free volume. It is considered that, upon a prolonged excitation, the vacancies are filled with coiled polymers and then the surface showed the protrusion. That is why the protrusion follows the appearance of the bright spot. This interpretation is consistent with the results showing that the width of the protuberance was narrower than that of the bright and dark spots, because the amount of coiled polymers decreases as the distance from the excitation spot increases.

The surface protrusion can also be patterned closely. Figure 4 shows a shear-force image of patterned protuberances. Each point was excited for 2 min with 1 mW. The protuberances were formed with a 600 nm spacing and patterned as letters “N” and “F”, whose sizes were smaller than 2 μm .

In conclusion, a direct correlation between the changes of the surface morphology, the polymer conformation, and the fluorescence spectrum in poly(substituted thiophene) film was made clear by the near-field fluorescence microspectroscopy techniques. We have found that a photothermally induced rod-

coil transformation leads to the nanoscale surface protrusion as well as the blue shift in the fluorescence spectrum. We have also found a time lag in appearance of the protuberance and the bright spot, indicating that an accumulation of coiled polymers above a certain critical density is necessary to induce the surface protrusion. These results indicate that the surface morphological change can be interpreted as a cooperative phenomenon of transformed polymers. The near-field microspectroscopic analysis as a function of the height/thickness or the surface morphology, which we put forward here, should be proved indispensable for studying nano-photoreactions on the surface.

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